THERMODYNAMIC PROPERTIES OF COMPRESSED LIQUIDS AND LIQUID MIXTURES FROM FLUCTUATION SOLUTION THEORY

BY

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF
THE UNIVERSITY OF FLORIDA IN PARTIAL
FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1986

To my parents and beloved sisters

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Dr. J.P O'Connell for his interest and guidance throughout the course of this study. He provides me with not only the kind of intellectual atmosphere that I have never experienced before but also many valuable opportunities to interact with some leading researchers in the field of fluid phase equilibria.

I also wish to thank Drs. G.B. Hoflund, W. Weltner, Jr. , S.O. Colgate, and G.K. Lyberatos for serving on the supervisory committee and Drs. E.A. Brignole and M.L. Michelsen for their helpful discussions.

Special thanks are due to professors A. Fredenslund and P. Rasmussen for their hospitality during my stay in the Instituttet for Kemiteknik, Danmarks Tekniske Højskole and Mr. R.P. Currier and Mr. T. Schmidt for their assistance during my stay in the Københavns Amts Sygehus I Gentofte.

It is a pleasure to thank Mrs. Sun for her excellent typing and patience with my manuscripts and Mr. B.A. Klein and Mr. C.T. Skowlund for their help in using VAX and UNIX computing systems.

Finally, I am grateful to the Northeast Regional Computing Center, Florida, for use of their facilities and Department of Energy, National Science Foundation and University of Florida for providing the financial support that made this work possible.

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KEY TO SYMBOLS

A = Helmholtz free energy

a_i = ith order reduced density coefficient of DCFI model

a_{ij} = coefficient matrix of DCFI model

b = constant

C = direct correlation function integral

c = molecular direct correlation function

C_p = heat capacity at constant pressure

d = effective hard sphere diameter

f = state dependent function

g = pair distribution function, state dependent function

H = enthalpy, spatial integrals of total correlation function

h = total correlation function

$\underline{I}$ = identity matrix

k = Boltzmann's constant

k_{ij} = binary parameter

M = general property

m = integer

N = number of moles, number of components

n = integer, refractive index

P = pressure

R = gas constant

$\vec{r}$ = position vector

S = entropy

$\vec{s}$ = position vector

T = temperature

U = internal energy

u = velocity of sound, intermolecular potential

V = volume

v = V/N, molar volume

$\bar{v}_i$ = partial molar volume of component i

$\underline{X}$ = matrix of mole fraction

x = mole fraction, position

Y = density dependent function of hard sphere diameter

α_p = isobaric expansivity

γ_i = activity coefficient of component i

γ_v = thermal pressure coefficient

δ = Kronecker delta

$\underline{\Theta}$ = parameter set

Θ_i = parameter of molecule i

$\theta = \varepsilon/kT$

ε = energy parameter, dielectric constant

η = packing fraction

κ_T = isothermal compressibility

μ = chemical potential

ν = Stochiometric coefficient

ρ = density

σ = collision diameter

τ = inverse of reduced temperature

φ_i = volume fraction of component i

Ω = orientation normalization factor

ω = angular orientation coordinate

Subscripts

c = critical property

i,j,k = component

ij,jk,ik = pairs of components

m = mixture

o = reference property, saturation property

hs = hard sphere

Superscripts

E = excess property

r = reference state

* = characteristic parameter

o = standard state

' = first composition derivative

" = second composition derivative

Special Symbols

_ (as in $\underline{X}$)	Matrix quantity
¯ (as in $\overline{v}$)	Partial molar property
~ (as in $\tilde{\rho}$)	reduced property
o (as in v_i^o)	pure component property

$\langle\ \rangle$	ensemble average
$\langle\ \rangle_{\omega}$	angular orientation average

Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

THERMODYNAMIC PROPERTIES OF COMPRESSED LIQUIDS AND LIQUID MIXTURES FROM FLUCTUATION SOLUTION THEORY

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August 1986

Chairman: John P. O'Connell
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For every pure liquid there exists a characteristic volume for which the reduced bulk modulus, $v/\kappa_T RT = (\partial(P/RT)/\partial\rho)_T$, is independent of temperature. In addition to the possible physical significance of this effect, the crossover point serves as the basis for a correlation of the spatial integrals of the statistical mechanical direct correlation function (DCFI) which can be related to the density derivatives of thermodynamic properties in the fluctuation solution theory.

The pressure variation of the volume and reduced bulk modulus of essentially all pure and mixed liquids are correlated with a three-parameter corresponding states correlation over temperatures from the triple to nearly the critical point and densities from the saturation to

the freezing point. The parameterization is based on the detailed analysis of the most accurate experimental data. The three parameters each serve a particular mathematical purpose, ensuring flexible and tractable numerical calculations.

The correlation method has been applied to over 200 pure and mixed liquids with errors probably within those of the experiments, making it significantly more general and accurate than previous models. The systems investigated cover all orders of complexity of molecular structure and intermolecular interaction. These include liquefied noble gases, short- and long-chain hydrocarbons, small and large globular chain or ring compounds, polar and highly associating species, metallic liquids, molten salts, and polymer melts. Mixtures of simple and complex systems are carefully examined.

The results are relatively insensitive to the characteristic temperature and all parameters may be estimated by a group contribution method. Simple mixing rules work successfully in a one-fluid form for mixtures with small excess volume. In other cases, a single binary parameter is adequate for good agreement. These findings indicate that the direct correlation function integrals are less sensitive to the exact details of the intermolecular forces for dense liquids than other statistical mechanical quantities.

This correlation, along with accurate saturation values, will provide all thermodynamic properties of compressed liquids and liquid mixtures.

CHAPTER 1
INTRODUCTION

High pressure liquids and liquid mixtures are present in many natural and man-made situations.[1] They vary from geological systems to high pressure processes and techniques. Thermodynamic properties of compressed liquids and their mixtures are important both in basic scientific research and practical engineering applications. Thus the theoretical study of the volumetric behavior of compressed liquids is motivated by the concept that the structure of dense liquids is dominated by the short-range repulsive forces and that their physical properties can be treated in terms of a hard sphere model.[2] From the practical point of view, liquid volumes are used exclusively in equipment sizing and descriptions of occupancy in natural reservoirs and formations.

Since the pioneering work of Bridgman,[3] there have been many volumetric measurements of compressed pure liquids, whereas much less effort has been dedicated to compressed liquid mixtures. A recent survey[4] of PVT properties of liquid and liquid mixtures listed about 350 pure components and 170 binary mixtures. However, half of the numbers cited are restricted to very limited pressure

or temperature ranges, including many of atmospheric or single isotherm measurements. Compression data of pure liquids have been correlated with equations such as those of Tait,[5] Hudleston,[6] Hayward,[7] Chaudhuri,[8] and others. Despite their substantial value for smoothing, interpolation, and computation of compressional thermodynamic functions, these equations share common disadvantages. First, they contain no explicit temperature dependence, so extensions by using temperature-dependent parameters are still uncertain. Second, two parameters are insufficient for wide pressure range isotherms, so extrapolations to either low or extreme high pressures are inaccurate. Third, their empirical nature renders molecular interpretation difficult. Fourth, these equations do not lead to mixing rules for compressed liquid mixtures.

An acceptable equation of state, apart from quantitative success, should provide some insight into the molecular characteristics in terms of a minimum possible set of parameters. Agreement between theory and experiment not only enhances one's faith in the molecular theory but also leads to the ability to generate the volumetric properties with confidence from very limited experimental efforts. Theoretical equations of state which are based on the modification of Prigogine's cell theory[9] such as Flory et al.,[10] Simha and Somcynsky,[11] and others have been applied to compressed liquids and liquid mixtures using scaling parameters evaluated from low-pressure density data.

However, as noted by Bridgman,[3] experimental behavior at low pressures is a poor guide to what is likely to happen at high pressure. As a result, these equations of state can not correctly represent the PVT behavior of compressed liquids at high pressure. Empirical modifications by Zoller,[12] and Simha and his coworkers[13-16] using elevated pressure data make only marginal improvement. Apparently, the theory cannot furnish an ideal representation of experimental PVT data at elevated pressure.

Recently, the Tait equation has been extended and generalized by Thomson et at.[17] This correlation, along with the correlation developed by Hankinson and Thomson[18] for saturated liquid densities, comprises the COSTALD method. These authors claim that COSTALD is the most general and accurate compressed liquid density correlation yet published. This is true when compared with those methods commonly used in chemical process calculations such as Yen-Woods,[19] Chueh-Prausnitz,[20] Lee-Kesler,[21] and others. However, the correlation method is purely empirical; application is limited to nonpolar and slightly polar liquids and pressures no higher than 700 bar.

A judicious alternative is to combine the simplicity of an empirical equation with the advantage of statistical mechanical theory in developing accurate and general relations for thermodynamic computations. Fluctuation solution theory is explored here for this purpose. The

basis of the method is from the statistical mechanical grand canonical ensemble which relates composition derivatives of the pressure and the chemical potential, thus the activity coefficient, to integrals of the molecular direct correlation function. As recognized by O'Connell,[22-23] and Gubbins and O'Connell,[24] the density dependence of the reduced bulk modulus behaves differently and quite simply in liquid phase compared to the gas phase, regardless of the complexity of the intermolecular forces. Hence, this work focuses on describing the liquid state alone.

The most surprising feature of the reduced bulk modulus versus reduced density plot is that there exists a unique point of crossover of the isotherms for all of the compressed liquids studied. This finding is obviously a most important contribution to any liquid state theory. In view of the well-known fact that it is density, not pressure, that is the key variable for compressed liquids, a corresponding states correlation, based on the density and temperature expansion of reduced bulk modulus, has been constructed to predict accurately the pressure effect on the compressional thermodynamic properties.

In the chapters that follow, detailed descriptions of the theoretical background, experimental observations, model development, and successful applications, including pure and mixed liquids are presented. Chapter 2 describes the fluctuation solution theory and how useful

thermodynamic properties are related to the statistical mechanical direct correlation function integrals. Chapter 3 displays the reduced bulk modulus for many compressed liquids, providing significant features that are further exploited. For compressed liquid mixtures, volumetric data are fully analyzed and deeper insights concerned with the excess properties are carefully evaluated. Chapter 4 is devoted to the process of model construction. It is demonstrated how the theoretical concept can be transformed into an actual working equation that simulates, to within experimental accuracy, the compressed liquid behavior. Chapter 5 applies the model to pure liquids. Also basic thermodynamic properties such as entropy, internal energy, and others are derived through the Maxwell relations. Characteristic parameters and comparison with a variety of pure liquids compression data are tabulated. An initial attempt at a group contribution correlation for the parameters is also given. Chapter 6 extends the model to liquid mixtures. Mixture properties such as partial molar volume, activity coefficient, and others are expressed in a one-fluid form. Binary parameters and comparison with liquid mixture compression data are tabulated. Chapter 7 closes this work with some remarks on the numerical techniques and our present concept of compressed liquid properties.

CHAPTER 2
FLUCTUATION SOLUTION THEORY FOR COMPRESSED LIQUIDS AND LIQUID MIXTURES

Introduction

Over the years there have been a growing number of uses of statistical mechanics in physical property research. There are two general approaches in the development of liquid state theory. One may be called the formal approach, based on distribution functions, while the other may be called the model approach, based on partition functions. The former was pioneered by Mayer and Mayer,[25] Kirwood,[26] and others. Thermodynamic properties can be calculated through the energy equation and the pressure equation with known pairwise additive potentials and pair distribution functions.[27] The latter approach visualizes a liquid with a certain physical picture, such as made up of cells,[28] holes,[29] or molecular arrangements. Thermodynamic properties then can be obtained by transforming these physical models into a partition function. All suffer the disadvantage of assuming pairwise additivity of intermolecular potentials.

Another alternative may be called the fluctuation solution theory.[24] The compressibility equation which relates concentration derivatives of pressure and

chemical potential to the spatial integrals of the total correlation function, and hence to direct correlation function integrals (DCFI) in the grand canonical ensemble is free from this assumption. Furthermore, the DCFI appear to be insensitive to the exact details of intermolecular forces. Therefore, from a numerical point of view, the theory involves integration of a simple model, instead of taking the derivative of a complicated expression as in the others. Experience shows that this should be less sensitive to errors of modeling. It is the number density and temperature, not the usual mole fraction, pressure, and temperatures that are the most appropriate set of independent variables for theoretical work. However, the equations allow for consistent relationships to be made among the variables.

Fluctuation Solution Theory and Direct Correlation Function Integrals

In the statistical mechanical grand canonical ensemble, a relation exists between composition fluctuations and derivatives of the mean composition with respect to chemical potentials.

$$\left.\frac{\partial \langle N_j \rangle}{\partial \mu_i / kT}\right|_{T,V,\mu_{k\neq i}} = \langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle \qquad (2\text{-}1)$$

where the brackets denote a grand canonical ensemble average. These averages are also related to the spatial integrals of the radial distribution function by

$$\langle N_i N_j \rangle - \delta_{ij}\langle N_i \rangle = \frac{\langle N_i \rangle \langle N_j \rangle}{V} \int g_{ij}(\vec{r})\, d\vec{r} \tag{2-2}$$

where δ_{ij} is the Kronecker delta. As recognized by Kirkwood and Buff,[30] $g_{ij}(\vec{r})$ is not necessarily limited to be the radial distribution functions for spherical molecules; it can also be interpreted as a more general pair distribution function with all possible orientations. Using the definition of total correlation function,

$$h_{ij} = g_{ij} - 1 \tag{2-3}$$

A combination of equations (2-1), (2-2), and (2-3) yields

$$\left.\frac{\partial \langle N_j \rangle}{\partial \mu_i / kT}\right|_{T,V,\mu_{k\neq i}} = \delta_{ij}\langle N_i \rangle + \frac{\langle N_i \rangle \langle N_j \rangle}{V} \int \langle h_{ij}(\vec{r}) \rangle_\omega \, d\vec{r} \tag{2-4}$$

where

$$\langle h_{ij}(\vec{r})\rangle_{\omega} = \frac{1}{\Omega^2}\int\int h_{ij}(\vec{r}\omega_i\omega_j)d\omega_i d\omega_j$$

= the angle averaged total correlation function.

$\Omega = \int d\omega$ = the nomalization constant of the orientation dependence.

$\vec{r} = \vec{r}_i - \vec{r}_j$ = the translational change of the position vector i and j.

Equation (2-4) can be written as

$$\left.\frac{\partial \rho_j}{\partial \mu_i/RT}\right|_{T,V,\mu_{k\neq i}} = \delta_{ij}\rho_i + \rho_i\rho_j \int \langle h_{ij}(\vec{r})\rangle_{\omega}\, d\vec{r} \qquad (2\text{-}5)$$

This is the basic equation of the Kirkwood-Buff solution theory.[30] From Orstein and Zernike,[31] the direct correlation function is defined as

$$C_{ij}(\vec{r}_i\vec{r}_j\omega_i\omega_j) = h_{ij}(\vec{r}_i\vec{r}_j\omega_i\omega_j) - \sum_k \rho_k \iint C_{ik}(\vec{r}_i\vec{r}_k\omega_i\omega_k)\, h_{kj}(\vec{r}_k\vec{r}_j\omega_k\omega_j)d\vec{r}_k d\omega_k \qquad (2\text{-}6)$$

The second term on the right-hand side represents the indirect correlations due to all possible third

molecules. Similarly, the angle averaged version of Equation (2-6) is

$$\langle C_{ij}(\vec{r})\rangle_\omega = \langle h_{ij}(\vec{r})\rangle_\omega - \sum_k \rho_k \int \langle C_{ik}(\vec{s})\rangle_\omega \langle h_{kj}(\overrightarrow{r-s})\rangle_\omega \, d\vec{s} \qquad (2\text{-}7)$$

where $\langle C_{ij}(\vec{s})\rangle_\omega = \frac{1}{\Omega^2} \iint C_{ij}(\vec{r}\omega_i\omega_j) d\omega_i d\omega_j$

= the angle averaged direct correlation function.

$\vec{s} = \vec{r}_i - \vec{r}_k$ = the translational change of position vector i and k.

$\overrightarrow{r-s} = \vec{r}_k - \vec{r}_j$ = the translational change of position vector k and j.

The angle averaging operation in the last term of Equation (2-7) may not be appropriate for long-range potentials.[32] Integration of Equation (2-7) yields

$$\rho \int \langle C_{ij}(\vec{r})\rangle_\omega \, d\vec{r} = \rho \int \langle h_{ij}(\vec{r})\rangle_\omega \, d\vec{r} - \rho^2 \sum_k x_k \iint \langle C_{ik}(\vec{s})\rangle_\omega \langle h_{kj}(\overrightarrow{r-s})\rangle_\omega \, d\vec{r} \, d\vec{s} \qquad (2\text{-}8)$$

In matrix notation, Equation (2-8) can be expressed as

$$\underline{C} = \underline{H} - \underline{C}\ \underline{X}\ \underline{H} \tag{2-9}$$

where $\underline{X}$ is a diagonal matrix whose nonzero elements are mole fractions. After basic matrix manipulations, Equation (2-9) can be written as

$$\underline{I} + \underline{H}\ \underline{X} = (\underline{I} - \underline{C}\ \underline{X})^{-1} \tag{2-10}$$

or

$$\delta_{ij} + \rho_i \int \langle h_{ij}(\vec{r})_\omega \rangle d\vec{r} = (\delta_{ij} - \rho_i \int \langle C_{ij}(\vec{r})_\omega \rangle d\vec{r})^{-1} \tag{2-11}$$

Comparing Equation (2-11) with Equation (2-5) and recognizing that the elements of the left-hand side of Equation (2-5) are the matrix inverse of a more desirable partial derivative,

$$\left.\frac{\partial \mu_i/RT}{\partial \rho_j}\right|_{T,\rho_{k\neq j}} = \frac{\delta_{ij}}{\rho_i} - \frac{C_{ij}}{\rho} \tag{2-12}$$

where $C_{ij} = \rho \int \langle C_{ij}(\vec{r}) \rangle_\omega \, d\vec{r}$ = the direct correlation function integrals. This is the basic connection between thermodynamic variables and direct correlation function integrals.

Thermodynamic Consequences

From the isothermal Gibbs-Duhem equation, the composition derivative of the pressure and the chemical potentials are related to each other by

$$\left.\frac{\partial P/RT}{\partial \rho_j}\right|_{T,\rho_{k\neq j}} = \sum_i \rho_i \left.\frac{\partial \mu_i/RT}{\partial \rho_j}\right|_{T,\rho_{k\neq j}} \qquad (2\text{-}13)$$

Substitution of Equation (2-12) into Equation (2-13) yields

$$\left.\frac{\partial P/RT}{\partial \rho_j}\right|_{T,\rho_{k\neq j}} = \sum_i x_i(1-C_{ij}) \qquad (2\text{-}14a)$$

$$= \frac{\bar{V}_j}{\kappa_{Tm}RT} \qquad (2\text{-}14b)$$

where the subscript m indicates mixture properties and κ_T is the isothermal compressibility. Summing all equations (2-14) yields

$$\left.\frac{\partial P/RT}{\partial \rho}\right|_{T,\,\underline{x}} = \sum_i \sum_j x_i x_j(1-C_{ij}) \qquad (2\text{-}15a)$$

$$= \frac{1}{\rho_m \kappa_{Tm} RT} \qquad (2\text{-}15b)$$

The partial molar volume $\bar{V}_j$ then can be expressed in terms of density and the DCFI

$$\bar{V}_j = \frac{\sum_i x_i(1-C_{ij})}{\rho_m \sum_i \sum_j x_i x_j (1-C_{ij})} \tag{2-16}$$

where ρ_m is mixture molar density. An isothermal change of pressure can be obtained by integration of Equation (2-14)

$$\frac{P-P^r}{RT} = (\rho-\rho^r) - \sum_j \int_{\rho_j^r}^{\rho_j} \sum_i \frac{\rho_i C_{ij}}{\rho} \Bigg|_{T,\rho_{i\neq j}} d\rho_j \tag{2-17}$$

while an isothermal change of chemical potential is

$$\frac{\mu_i-\mu_i^r}{RT} = \ln \frac{\rho_i}{\rho_i^r} - \sum_j \int_{\rho_j^r}^{\rho_j} \frac{C_{ij}}{\rho} \Bigg|_{T,\rho_{k\neq j}} d\rho_j \tag{2-18}$$

where the superscript r denotes a reference property. This can be any fluid state, including ideal gas, saturation, or other well-determined conditions. Naturally, the model for the C_{ij} must be appropriate over the entire range of the integration. In phase equilibrium calculations, it is usually more convenient to work with activity coefficient than chemical potential.

$$\mu_i(T,\underline{\rho}) = \mu_i^o(T,\underline{\rho}^r) + RT\ln x_i\gamma_i(T,\underline{\rho}) \qquad (2\text{-}19)$$

where the superscript o denotes the standard state properties. Substitution of Equation (2-19) into Equation (2-12) yields

$$\left.\frac{\partial \ln\gamma_i}{\partial \rho_j}\right|_{T,\rho_{k\neq j}} = \frac{1-C_{ij}}{\rho} \qquad (2\text{-}20)$$

Composition integration of equation (2-20) yields

$$\ln \frac{\gamma_i}{\gamma_i^r} = \sum_j \int_{\rho_j^r}^{\rho_j} \left(\frac{1-C_{ij}}{\rho}\right) d\rho_j \qquad (2\text{-}21)$$

For a pure component,

$$\left.\frac{\partial P/RT}{\partial \rho}\right|_T = 1 - C \qquad (2\text{-}22a)$$

$$= \frac{1}{\rho\kappa_T RT} \qquad (2\text{-}22b)$$

This is the reduced bulk modulus of pure liquids, the quantity of primary interest in the present work.

CHAPTER 3
VOLUMETRIC BEHAVIOR OF COMPRESSED LIQUIDS AND LIQUID MIXTURES

Introduction

Theoretical investigations of the physical properties of dense liquids indicate that the structure of liquids, static or dynamic, is similar to that of a rigid-body system. In order to examine the effects of the differences between real and rigid-body systems, the temperature and density effects should be separated requiring experimental studies at high pressures. In describing the thermodynamic state of a liquid, the applied pressure is considered high if it is comparable to or greater than the kinetic pressure.[33] The thermodynamic equation of state is

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T \qquad (3\text{-}1)$$

where the thermal pressure coefficient, $T\left(\frac{\partial P}{\partial T}\right)_V$, is the kinetic pressure resulting from the molecular motion and the energy-volume coefficient, $\left(\frac{\partial U}{\partial V}\right)_T$, is a measure of the internal pressure arising from the intermolecular forces. When the energy-volume coefficient $\left(\frac{\partial U}{\partial V}\right)_T$ is zero, the external pressure P is equal to the kinetic pressure $T\left(\frac{\partial P}{\partial T}\right)_V$, and

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T} \qquad (3\text{-}2)$$

This is the case for a rigid-body fluid. When the applied pressure P is close to the kinetic pressure, a perturbation approach is suggested using a rigid body reference with a small perturbation attractive potential term. Under these circumstances, the volume plays the dominant role in affecting the molecular behavior in liquids, because the molecules are so closely packed together that the forces between them arise almost exclusively from the short-range repulsive forces.

There has been much theoretical speculation concerning this physical picture of liquids. The first controversy comes from the experimental evidence that the internal energy passes through a minimum which is characteristic of the liquid and a function of temperature.[34] This brings in a temperature dependent effective hard-core diameter which would be necessary to make Equation (3-2) behave like Equation (3-1). Further experimental evidences for highly compressed liquids indicate that theoretical values of the hard sphere liquid deviate systematically from the experimental values.[35] This suggests that the effective hard-core diameter becomes density dependent at high packing fractions ($\rho\sigma^3 > 0.93$) due to the softness of the repulsive potential and/or orientational ordering in compressed liquids. Figure 3-1 shows the reduced bulk modulus of a hard sphere liquid calculated

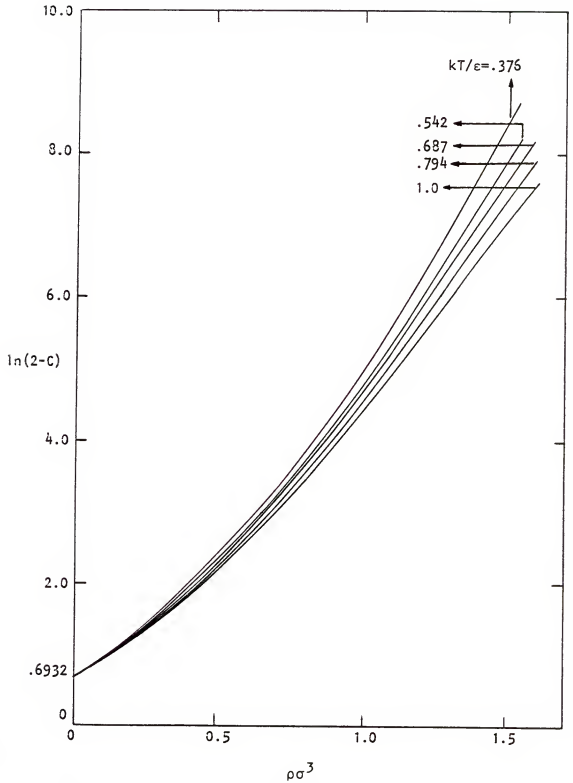

Figure 3-1. Theoretical DCFI of Effective Hard Sphere Liquid

from the Percus-Yevick compressibility equation. The Verlet-Weis algorithm is adopted to simulate the temperature and density dependent effective hard-core diameters of Weeks-Chandler-Andersen perturbation theory.[2] Detailed calculations are summarized in Appendix A. Figure 3-2 shows the experimental reduced bulk modulus of liquid argon calculated from Twu's algorithm.[36] Comparison of Figures 3-1 and 3-2 shows that the differences are significant, especially at high pressure where the crossover is observed for argon and the temperature dependence is very small.

Since theoretical calculations of compressed liquids are improbable, the alternative is to analyze fully the experimental data available and develop an empirical relationship. There are several interesting findings concerning the volumetric behavior of compressed liquids and liquid mixtures. The earliest one is made by Bridgman on the pressure effect of isobaric expansivity.[3] At low pressure, the thermal expansion coefficient of liquids increases with rising temperature. At high pressure, this relation is reversed. The reversal in the sign of the temperature derivative of isobaric expansivity is due to the nonlinear effect of the intermolecular forces. It is interesting to relate this phenomenon to the behavior of constant pressure heat capacity.[3]

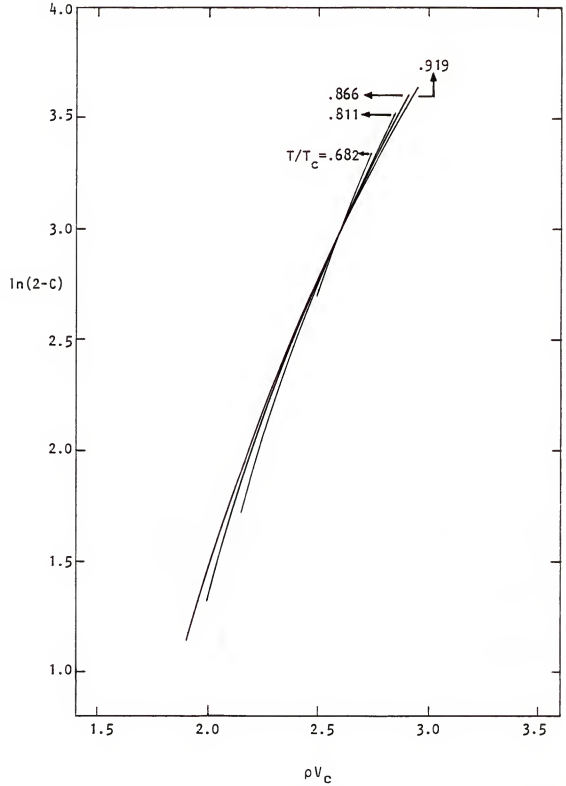

Figure 3-2. Experimental DCFI of Liquid Argon

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{3-3a}$$

$$= -VT\left(\alpha_P^2 + \frac{d\alpha_P}{dT}\right) \tag{3-3b}$$

where α_P is the isobaric expansivity. The effect found by Bridgman raised the possibility of a minimum in C_P as a function of pressure.

Similar observations on the change of internal energy with pressure were also made by Bridgman.[3]

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T \tag{3-4}$$

The pressure at which the left-hand side of (3-4) is zero is given by the same form as Equation (3-2).

$$P = \frac{-T\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V \tag{3-5}$$

These variations were further explored by Jenner and his coworker[37-40] on the compression measurement of 1-bromoalkanes from C_2 to C_7 in the liquid state. The applied pressure is up to 6 Kbar in the temperature range between 203°K and 448°K. For all of the bromides

investigated, there exists a well-determined pressure for which the isobaric expansivity is independent of temperature. This inversion pressure is further confirmed by experimental data from the piezothermal method of Ter Minassian and his coworkers[41,42] on liquid water, carbon dioxide, and n-butane. The curves of the pressure derivatives of internal energy and of heat capacity show similar behavior as a function of pressure. In addition to the observed minimum at different temperatures, all of the isotherms pass through a single point at the inversion pressure noted above. Further, the isothermal variation of the heat capacity difference C_p-C_V exhibits the same crossover at the inversion pressure.

In all of these cases, there must exist a thermodynamic relationship at the inversion pressure p_i. First,

$$\frac{d\alpha_{Pi}}{dT} = \frac{1}{V}\left(\frac{\partial^2 V}{\partial T^2}\right)_{Pi} - \alpha_{Pi}^2$$

$$= 0 \qquad (3\text{-}6)$$

leading to

$$\alpha_{Pi}^{*} = \left[\ \frac{1}{V}\left(\frac{\partial^2 V}{\partial T^2}\right)_{Pi}\ \right]^{1/2} \qquad (3\text{-}7)$$

Second,

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{Pi}$$

$$= b_1 \qquad (3\text{-}8)$$

where b_1 is a constant. Combination of Equation (3-7) and (3-8) yields

$$TV = -\frac{b_1}{\alpha^{*2}_{Pi}} \qquad (3\text{-}9)$$

Third,

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_{Pi}\left(\frac{\partial P}{\partial T}\right)_V$$

$$= TV\alpha^*_{Pi}\,\gamma_V$$

$$= -\frac{C_1}{\alpha^*_{Pi}}\gamma_V$$

$$= b_2 \qquad (3\text{-}10)$$

where b_2 is another constant. From Equation (3-10), the thermal pressure coefficient γ_V can be written as

$$\gamma^*_V = -\frac{b_2}{b_1}\,\alpha^*_{Pi} \qquad (3\text{-}11)$$

From the triple product rule, the isothermal compressibility κ_T can then be given as

$$\kappa_T^* = \frac{\alpha_{P_i}^*}{\gamma_V^*}$$

$$= - \frac{b_1}{b_2} \qquad (3\text{-}12)$$

This is true only when inversion pressures are exactly the same for all of the properties investigated above. Unfortunately, data analysis on the isothermal compressibility is unavailable in Jenner's work to confirm this completely. Careful analysis of this property will be described in next section.

Pure Liquids

Volumetric properties of large globular and long-chain hydrocarbons have been measured by Grindley[43] for temperatures from 298°K to 453°K and pressures from zero to 8 Kbar. The data are adequate to determine the first and second volume derivatives of the internal energy and entropy. The first isothermal volume derivatives yield the thermodynamic equation of state.

$$P = T\left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial U}{\partial V}\right)_T \qquad (3\text{-}13)$$

Both terms on the right-hand side of (3-13) are temperature dependent. However, scaling can be achieved by a two-parameter corresponding states relation. The second

isothermal volume derivatives are related to the bulk modulus

$$\frac{1}{RT\kappa_T} = \frac{V}{RT}\left(\frac{\partial^2 U}{\partial V^2}\right)_T - \frac{V}{R}\left(\frac{\partial^2 S}{\partial V^2}\right)_T \qquad (3\text{-}14)$$

In contrast to the external pressure expression (3-13), where the entropy term dominates throughout the whole density region, the bulk modulus has a large contribution from both terms. The entropy term is larger at low densities while the energy term is larger at high densities. This can be seen clearly from Figure 3-3 for the second isothermal volume derivative properties of n-nonane. The crossing of the bulk modulus isotherms is due to the additive effect of both entropy and energy term, though crossing of the energy term also appears at higher densities.

The thermodynamic implications of this behavior have been analyzed further in this work. Our examination of the experimental reduced bulk modulus data available reveals a similar feature: A density at which the reduced bulk modulus, which is related to the integral of the direct correlation function of Chapter 2, is independent of temperature. Figure 3-4 shows the experimental behavior of the DCFI for methane from Mollerup's computer programs.[44] At the critical point, the DCFI is unity because the reduced bulk modulus is zero. At the ideal gas limit, the DCFI is zero, and hence the reduced bulk

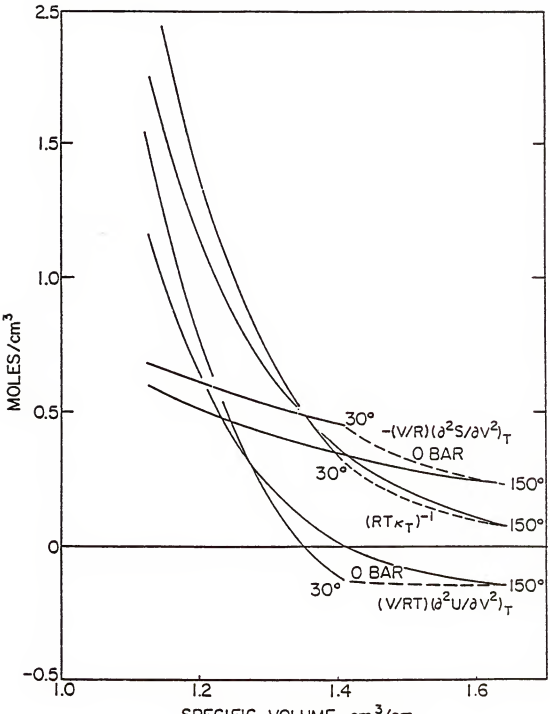

Figure 3-3. Entropy and Energy Contributions to the Bulk Modulus of n-nonane

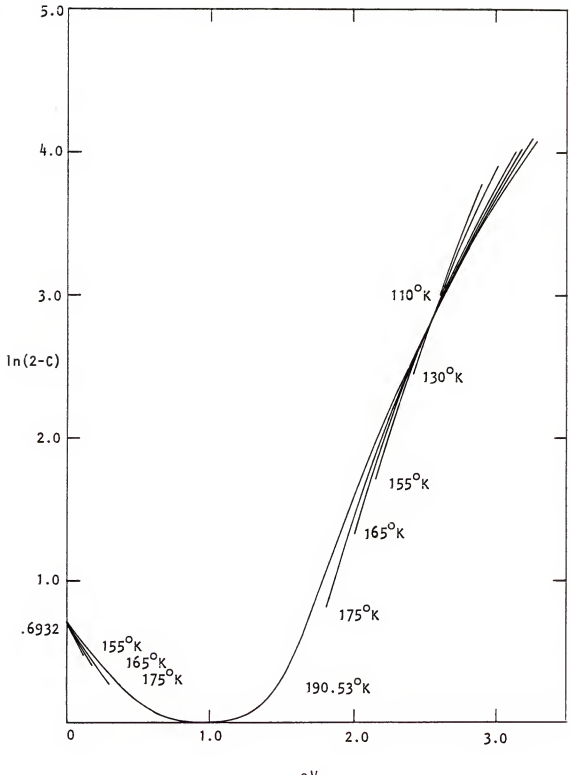

Figure 3-4. Experimental DCFI of Liquid Methane

modulus is unity. Generally, the DCFI is small and positive (less than unity) in the vapor phase; it is large and negative in the liquid phase. The high density limits of the isotherms are the freezing line, while the low density limits of the liquid isotherms are the saturated liquid. Figures 3-5 and 3-6 show the DCFI of two sets of isomers: n-nonane, 3,3-diethylpentane, and n-heptadecane, 5,5-dibutylnonane in the liquid state alone. All the experimental curves behave similarly with relative insensitivity to the temperature in the higher density range, and the crossover is apparent. By shifting the curves to superimpose the crossover DCFI and density, complete overlap can be obtained by rotating the graphs slightly to bring the isotherms into coincidence. This provides the basis for a three-parameter corresponding state correlation of the reduced bulk modulus. Similar behavior has been found for essentially every other substance studied except water. Figure 3-7 shows the DCFI of water generated from the computer programs of the National Bureau of Standards.[45] The temperatures are from boiling to the critical point and pressures up to 10 Kbars. Except for the low temperature isotherms (below 50°C), water exhibits the same volumetric behavior as the other substances over a very broad range of state conditions. The differences at low temperature can be attributed to hydrogen bonding which decreases rapidly with temperature, a conclusion which has been reached on evidence from diverse sources.[46]

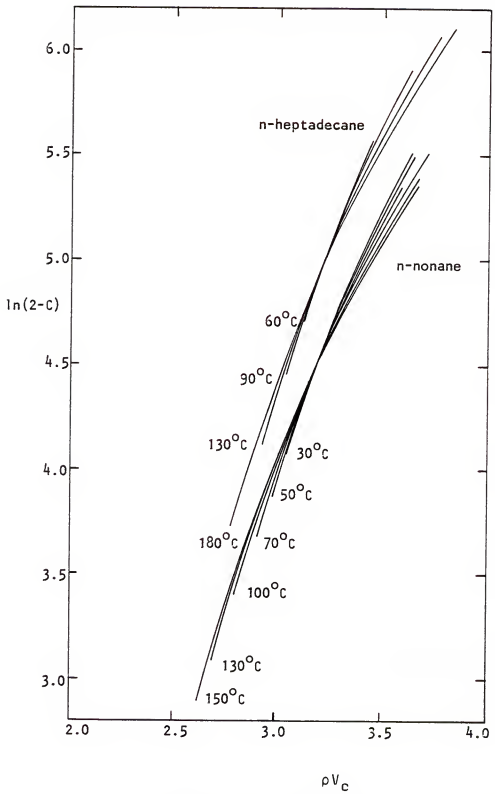

Figure 3-5. Experimental DCFI of Liquid n-nonane and n-heptadecane

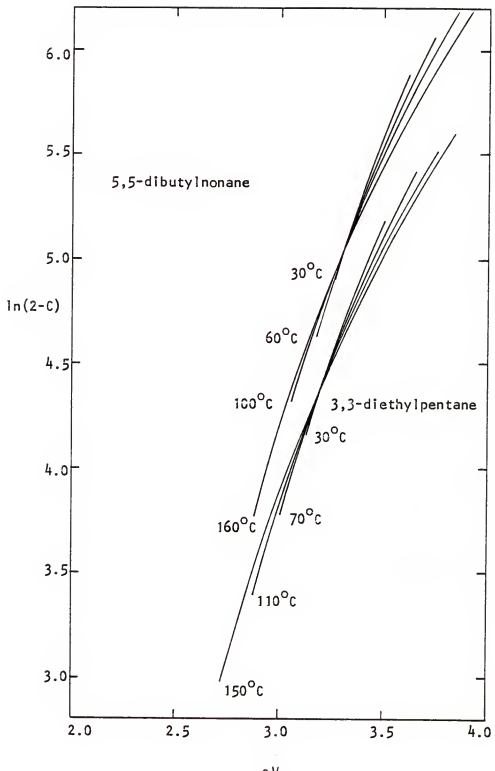

Figure 3-6. Experimental DCFI of 3,3-diethylpentane and 5,5-dibutylnonane

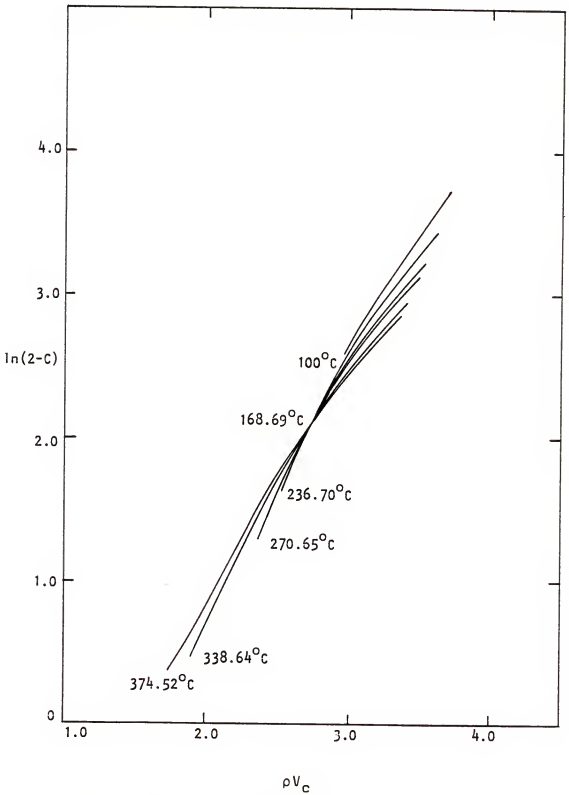

Figure 3-7. Experimental DCFI of Liquid Water

Volume and temperature have been chosen as the independent variables since they are the most suitable for theoretical treatment. In general, volume scaling is the result of an increase in molecular size, while temperature scaling is due to the ratio of potential to kinetic energy effects and variation in rotational degrees of freedom. The relative insensitivity of the DCFI with temperature in the compressed state indicates that internal degrees of freedom are not appreciably altered when the density changes above twice the critical density. The crossover reduced bulk modulus variation which leads to DCFI scaling arises probably from the combined effects of size and intermolecular forces because of the additive effects of entropy and energy contributions to the crossing of the liquid bulk modulus. To better understand this conjecture, two separate studies from Gibson and Loeffler[47] and Grindley and Lind[48] can be considered. For the same sized molecules, if a polar group is introduced as in the former case, or upon charging a set of neutral molecules to form a molten salt as in the latter case, the major contribution to the decreased pressure and isothermal compressibility (or increased DCFI) comes from an increased $(\frac{\partial U}{\partial V})_T$ which makes $(\frac{\partial^2 U}{\partial^2 V^2})_T$ more positive. Only a small contribution comes from a decrease of $(\frac{\partial S}{\partial V})_T$ and $(\frac{\partial^2 S}{\partial V^2})_T$.

Liquid Mixtures

Insights into the thermodynamic properties of liquid mixtures can be obtained from the excess volume as a function of pressure, temperature and composition. An equation of state based on the excess volume V^E can be written as

$$V_m(T,P,\underline{x}) = \sum_i x_i V_i^o(T,P) + V^E(T,P,\underline{x}) \qquad (3\text{-}15)$$

where V_m is the mixture volume and V_i^o is the volume of pure component i. The absolute value of excess volume is small in comparison to the mixture volume itself, whereas the variations of the excess volume with pressure, temperature and composition can be important and comparable to those of the mixture volume.

$$-\left.\frac{\partial V^E}{\partial P}\right|_{T,\underline{x}} = V_m \kappa_T^E \qquad (3\text{-}16)$$

$$\left.\frac{\partial V^E}{\partial T}\right|_{P,\underline{x}} = V_m \alpha_P^E \qquad (3\text{-}17)$$

and for binary mixtures,

$$\left.\frac{\partial V^E}{\partial x_1}\right|_{T,P} = \frac{1}{x_2}(\bar{V}_1 - V_m) + V_2^o - V_1^o \qquad (3\text{-}18a)$$

$$= \frac{1}{x_1}(V_m - \bar{V}_2) + V_2^o - V_1^o \qquad (3\text{-}18b)$$

$$\left.\frac{\partial V^E}{\partial x_2}\right|_{T,P} = \frac{1}{x_1}(\bar{V}_2 - V_m) + V_1^o - V_2^o \qquad (3\text{-}19a)$$

$$= \frac{1}{x_2}(V_m - \bar{V}_1) + V_1^o - V_2^o \qquad (3\text{-}19b)$$

Since very few measurements have been made to determine the equation of state for liquid mixtures, significant progress in their high pressure thermodynamics has not occurred. However, it is known that the experimental behavior of the excess volume as a function of temperature and composition is exceedingly complicated due to a variety of physical effects and intermolecular interactions. One behavior of interest is the pressure dependence of the excess volume of liquid mixtures. Figure 3-8 shows the excess volumes of the carbon monoxide-methane system from Calado et al.[49] and the n-heptane-ethanol system from Ozawa et al.[50] The absolute value of $(\frac{\partial V^E}{\partial P})_{T,\underline{x}}$ rapidly decreases with pressure, implying that high pressure mixtures for a wide variety of liquids show more ideal volumes of mixing than do low pressure systems. Generally, the pressure influence is very significant. For simple liquid mixtures, the excess volume is small and negative at low pressure, becoming almost zero at high pressures. For n-alkane mixtures, the excess volume is negative at low pressure, but it eventually

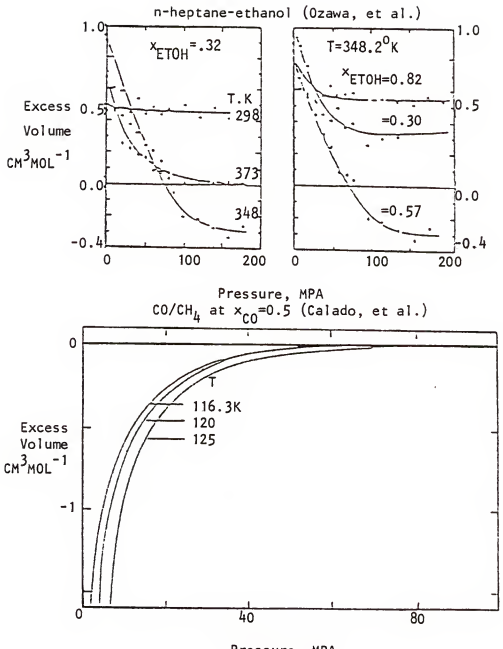

Figure 3-8. State Dependence of Excess Volume

becomes small and positive at high pressures. For n-alkane and 1-alkanol mixtures, the excess volume is positive at low pressures becoming negative at high pressures. For aqueous systems, the excess volume is large and negative at low pressures, becoming small and positive at high pressures. These are all closely related to the packing effect at highly compressed states.

CHAPTER 4
CORRESPONDING STATES CORRELATION FOR THE DIRECT CORRELATION FUNCTION INTEGRALS

Introduction

The practical value of the rigorous formulas derived in Chapter 2 and experimental observations discussed in Chapter 3 depends on a mathematical function to simulate the DCFI behavior. The ideal model for DCFI would yield a robust mathematical form, giving all of the variations nature shows with a minimum of experimentally accessible parameters that depend only weakly on thermodynamic states. Treatments using the corresponding states principle (CSP) have this desirable feature. However, most corresponding states correlations are based on the critical properties and other macroscopic fluid measurements such as saturation properties, so they are limited to classes of substances that have simple intermolecular forces. Furthermore, these properties are not always measurable as in the case of heavy hydrocarbons and coal liquids. However, a corresponding states correlation for the DCFI would be very useful in chemical process calculations if suitable parameters are found. In this chapter, a three-parameter corresponding states correlation has been developed to describe the DCFI of all liquids. The

three characteristic parameters of the correlation are the volume, V*, and DCFI, C*, at the crossover of the isotherms along with a temperature, T*, which is in the range of the critical temperature.

Model Development

The first apparent utility of the DCFI to describe the relationship of pressure and density for liquids was described by Brelvi[51] and Brelvi and O'Connell.[52-53] They noted that density, not temperature, was the dominant variable and the DCFI of many substances could be correlated in a one-parameter corresponding states form. In principle, their characteristic volume parameter could be determined from a single compression measurement. This correlation holds within 5-10% for a variety of substances over the dense liquid region. However, the correlation is uncertain at lower densities where the experimental data are sparse and temperature effect becomes significant. Further examination by Mathias and O'Connell[54-55] showed that the temperature dependence could be taken into account with a characteristic temperature in a two-parameter corresponding states form. Since temperature dependence was included, the results at low densities were improved. Unfortunately, the correlation used hard sphere expres-sions corrected by a linear density term so applications to high pressure were not of high accuracy.

In the present work, liquid compression data have been analyzed even more carefully and the most general form of the corresponding states relation is shown in Figure 4-1. The behavior of the liquid DCFI for methane is plotted in reduced coordinates along with some extensions using data for n-heptadecane. At the crossover point, the reduced density and DCFI are defined to be unity. While variations away from this characteristic density and DCFI are somewhat dependent on the temperature, they can be correlated in reduced form.

Model Parameterization

The present correlation takes advantage of the similarity of the crossover behavior that all dense liquid DCFI data show. The success of the model relies on the construction of an equation of state that can describe the reference substance accurately. Since this work has been concerned with formulating the thermodynamic properties of petrochemicals and coal-derived liquids, methane is used as the reference substance. The basic form of the correlation is chosen to express the reduced DCFI, $\tilde{C}=C/C^*$, as the polynomial expansions of the reduced density, $\tilde{\rho}=\rho V^*$, and the inverse reduced temperature, $\tilde{\tau}=T^*/T$.

$$\tilde{C} = \sum_{i=1}^{m} \sum_{j=1}^{n} a_{ij} (\tilde{\tau})^{j-1} (\tilde{\rho})^{i-1} \qquad (4\text{-}1)$$

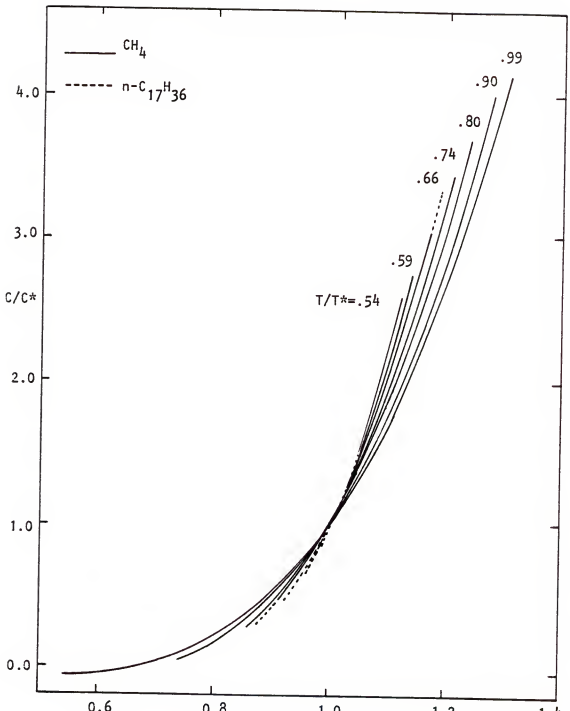

Figure 4-1. Corresponding States Correlation of Liquid DCFI

where a_{ij} is the coefficient matrix of the reduced variables.

After a thorough test using the liquid DCFI data of methane generated from Mollerup's computer program, the optimal expression has been determined as the lowest order polynomial that can achieve the same accuracy as his equation. In this case, m=4 and n=3. The coefficient matrix a_{ij} of equation (4-1) is given in Table 4-1. The agreement with experimental data overall is better than 0.2% except for low density points near the critical isotherms. The valid range of the reduced variables is $0.7 \leq \rho V^* \leq 1.3$ and $0.5 \leq T/T^* \leq 0.99$. This range could be expanded by use of a modified form of the polynomial and data for substances at lower reduced temperatures and higher reduced densities. These coefficients give the crossover value of $\tilde{C}=1$ to within 1% over the specified temperature range. The reduced bulk modulus then can be written as

$$\left.\frac{\partial P/RT}{\partial \rho}\right|_T = \frac{1}{\rho \kappa_T RT}$$

$$= 1 - C^* \tilde{C} \qquad (4\text{-}2)$$

Results and Discussions

Equation (4-1) with the coefficient matrix of Table 4-1 has been applied to all of the substances for which liquid DCFI data have been found. The compressibilities

TABLE 4-1

Coefficient Matrix a_{ij} for Equation (4-1)

m \ n	1	2	3
1	9.8642	-10.191	-1.5356
2	-28.465	30.864	6.0294
3	27.542	-32.898	-8.7130
4	-8.2606	12.737	4.0170

are generally from fitting volume changes with pressure and sonic velocities. The present reduced bulk modulus data bank includes 33 substances ranging from noble gases to petrochemicals to water and methanol. (Compressions of many more substances are discussed in Chapter 5.) Table 4-2 lists all of the characteristic parameters and the data ranges from which the parameters are evaluated. The values of V* are about 30-40% of the critical volume while the values of T* are normally within 20% of the critical temperature. The values of C* vary from -7 for very small molecules to -167 for large polyatomics. The results are in excellent agreement with the experimental data. For some substances with wide data ranges, the fitted pair parameters coincide with the crossover point observed experimentally. For substances with lower pressure ranges, the fitted pair parameters are close to the crossover point obtained from graphical extrapolation of the experimental results. This is also true when water is considered individually at high and low temperatures. There are two sets of characteristic parameters for water at different temperature ranges. They are listed separately because water behaves unusually at low temperatures[56] (below 75°C).

Discussion of the results can be developed according to the complexity of the substance, the range of the state conditions, and the accuracy of the experimental results.

Table 4-2

Characteristic Parameters and Comparisons with Liquid DCFI Data

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
Argon	19.0696	28.2294	139.854	0.5530	43	90-140	25.23-2497	36
Krypton	16.2128	35.2617	201.966	1.0809	28	120-200	25.33-3040	56
Xenon	16.4803	45.3441	277.367	0.7612	31	170-260	25.33-2533	57
Nitrogen	16.9860	34.6485	119.965	0.4628	20	77-101	21.37-519.4	58
Oxygen	20.3201	27.6618	146.000	0.2665	17	90-118	11.29-504.3	58
Methane	14.7575	38.7154	190.573	0.1835	77	95-185	0.65-4785	44
Ethylene	24.2217	47.8650	261.171	0.8795	43	160-250	5-1100	59
Ethane	27.7190	53.0997	295.785	0.9608	45	160-260	6.34-743.8	60
Propane	30.0627	71.7628	340.923	0.9285	56	200-320	0.2-711.6	61
n-Butane	32.9989	90.3628	391.759	0.9298	32	240-360	0.24-717.4	62
Isobutane	32.1510	91.7398	379.441	0.8390	32	240-360	0.4-711.1	63
n-Hexane	59.6000	122.802	454.693	0.9387	24	273-333	0-5018	64
n-Nonane	79.5211	174.750	508.562	1.3717	34	303-423	0-6000	43
n-Decane	98.2235	190.584	541.824	2.4417	32	298-358	1.01-5171	65
n-Dodecane	119.925	223.532	540.761	2.3157	32	298-358	1.01-4137	65
n-Hexadecane	167.000	288.290	522.111	1.4783	26	298-358	1.01-2757	65
n-Heptadecane	129.582	315.920	603.156	0.9444	29	333-453	0-8000	43

Table 4-2 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	P,bar	Ref.
3,3-Diethyl-pentane	76.0363	169.647	594.818	2.0520	31	303-423	0-8000	43
4,4-Dipropyl-heptane	99.1199	241.133	611.932	0.9592	30	303-373	0-5000	43
5,5-Dibutyl-nonane	134.342	308.186	624.183	1.5203	31	303-433	0-8000	43
Benzene	40.5966	88.5489	492.013	0.4674	24	298-358	0-1000	47
Chloro-benzene	42.7971	105.199	546.936	0.2961	24	298-358	0-1000	47
Bromobenzene	44.9976	109.707	564.097	0.2836	24	298-358	0-1000	47
Nitrobenzene	51.8347	108.264	582.678	0.3171	24	298-358	0-1000	47
Aniline	51.6100	96.0762	573.472	0.2393	24	298-358	0-1000	47
Carbon tetra-chloride	44.1436	95.0715	486.377	0.4886	24	298-358	0-1000	66
Ethylene glycol	33.9809	59.6111	603.269	0.2354	24	298-358	0-1000	66
Methanol	15.9110	39.7147	481.700	1.1346	68	298-473	0.17-1000	67
Water	15.7897	17.9400	298.093	0.8414	24	298-358	0-1000	66
	7.19912	20.1522	445.452	1.8048	42	348-573	0.39-1000	45

Table 4-2 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
Tetraethyl-silane	94.0941	183.536	510.458	2.5058	32	303-423	0-8000	43
Tetraethyl-ammonium tetrapropyl-borate	96.8865	198.677	695.258	0.5314	40	363-403	0-4200	43
Tetrapropyl-ammonium tetraethyl-borate	69.1909	204.873	836.801	0.8200	16	393-433	0-1400	43
Tetrabutyl-ammonium tetrabutyl-borate	146.013	299.692	716.369	0.7023	20	393-433	0-5000	43

In the case of monatomic substances from Streett et al.[56,57] and diatomic species from Bender,[58] the temperature ranges from just above the triple point to near the critical point, and pressures from saturation to freezing point. The agreement with the present correlation is within 1%. The ratios of the characteristic parameters to the critical properties are slightly lower than the reference methane values, while the characteristic DCFI values, -C*, are slightly higher. In the case of short-chain hydrocarbons from the National Bureau of Standards,[60-63] the reduced temperature range is between 0.5 and 0.97, and the pressures are from saturation to 700 bars. The agreement with the present correlation is within 1%. The ratio of the characteristic volume to critical volume is about 0.35 and the ratio of the characteristic temperature to critical temperature is about 0.92. In the case of long-chain hydrocarbons from Snyder and Winnick,[65] the temperatures are 25° to 85°C and pressures from about 1 bar to over 5 Kbars or the freezing pressure, whichever is lower. The agreement with the present correlation is within 2.5%. This is the worst for all of the substances tested. However, examination of the deviation patterns indicate that the major source of the disagreement comes from the atmospheric measurements of each isotherm. There are several possibilities related to this observation. First, the extrapolation of high pressure data to atmospheric pressure either by a graphic technique or by a

specific equation may cause errors, though it is a common practice in high pressure work. Second, the adoption of the atmospheric measurements from the other sources may cause inconsistency in the complete data set. Third, the initial compressibility of the long-chain hydrocarbons may behave differently from that of methane. If the deviations do result from the experimental uncertainty of the atmospheric DCFI, then the agreement with the present correlation is definitely within the experimental errors. Similarly, for long chain and large globular hydrocarbons of Grindly,[43] the temperatures are from 25° to 190°C and pressures from zero to 8 Kbars. The agreement with the present correlation is within 2%. The experimental precision of the lowest pressure compressibilities is only 1 or 2%, while above 400 bars, the precision is about .5%. Comparisons of the experimental data with the calculated results indicate that the deviation patterns are consistent with the previous assertions that the disagreement between the experimental DCFI and the present correlation at zero pressure is due to the experimental uncertainty at this state. For these larger hydrocarbons, the ratio of the characteristic to critical volume is about 0.31 and the ratio of the characteristic to critical temperature is between 0.8 and 0.9. The only exception is 3,3-diethylpentane which has an unusually high ratio of the characteristic to critical temperature; this is associated with the abnormally large disagreement of DCFI at zero pressure

where the temperature effect is significant. For benzene and some of its derivatives, the work of Gibson and Loeffler,[47,66] is ranked as one of the most accurate among all high pressure measurements. The temperatures are from 25° to 85°C and pressure from zero to 1 Kbars. The agreement with the present correlation is within 0.5% which is significantly better than for the rest of the substances. This is partly due to the insensitivity of the experimental DCFI with temperature at low pressures for these substances. Figure 4-2 shows the experimental behavior of DCFI for benzene. The value of -C* increases from liquid to liquid in the order of benzene, chlorobenzene, bromobenzene, nitrobenzene and aniline. This is consistent with the argument in the previous chapter that the introduction of a polar group acts on the liquid DCFI of benzene in the same way as the increase of energy volume coefficient. It changes the attractive potential and makes $(\frac{\partial^2 U}{\partial V^2})_T$ more positive. The ratio of the characteristic to critical volume is about 0.34 and characteristic to critical temperature is about 0.85. In the case of the molten salts from Grindly,[43] the temperatures are from 90° to 160°C and pressures from zero to 5 Kbars. The agreement with the present correlation is within 0.8%. The ratio of the characteristic to critical volume is about 0.32 and characteristic to the estimated critical temperature is about 1. Comparison of -C* values for

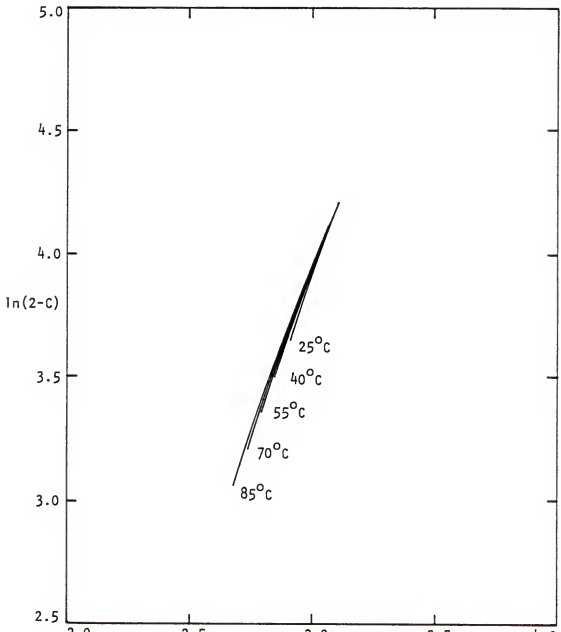

Figure 4-2. Experimental DCFI of Liquid Benzene

tetrabutylammonium tetrabutylborate and 5,5-dibutylnonane which have nearly the same V* confirms that the charges have the same effect on liquid DCFI as a polar group does. For highly associating species such as water[45,66] and methanol[67] the agreement with the present correlation over a broad range of state conditions is as good as the other substances; only lower temperature water is anomalous.

CHAPTER 5
APPLICATION OF THE MODEL TO OTHER PURE LIQUIDS

Introduction

Thermodynamic properties of a pure liquid can be calculated from the DCFI model using the parameter developed in the last chapter. In addition to isothermal compressibilities, there are compression data at high pressures, so model parameters based on the pressure equation and compression data can be obtained for these substances as well. These parameter tables include almost all of the significant liquid compression data available. The crossover parameters appear to be group additive and related to critical properties. Some of the group parameters for characteristic volume V* and characteristic DCFI C* are tabulated.

Derived Thermodynamic Properties

Isothermal integration of the DCFI model from a reference density, ρ_o to final density, ρ, yields the pressure, P

$$P = P_o + \rho^*RT\{(\tilde{\rho}-\tilde{\rho}_o)-C^*[(9.8642-\frac{10.191}{\tilde{T}}-\frac{1.5356}{\tilde{T}^2})(\tilde{\rho}-\tilde{\rho}_o)-$$

$$(14.2325-\frac{15.432}{\tilde{T}}-\frac{3.0147}{\tilde{T}^2})(\tilde{\rho}^2-\tilde{\rho}_o^2)+(9.18067-\frac{10.966}{\tilde{T}}-\frac{2.90433}{\tilde{T}^2})$$

$$(\tilde{\rho}^3-\tilde{\rho}_o^3)-(2.06515-\frac{3.18425}{\tilde{T}}-\frac{1.00425}{\tilde{T}^2})(\tilde{\rho}^4-\tilde{\rho}_o^4)]\} \qquad (5\text{-}1)$$

where P_o is the pressure at ρ_o and T. Substitution of the DCFI model into Equation (2-22b) yields the liquid bulk modulus κ_T^{-1},

$$\kappa_T^{-1} = \rho RT\{1-C^*[(9.8642-\frac{10.191}{\tilde{T}}-\frac{1.5356}{\tilde{T}^2})-(28.465-\frac{30.864}{\tilde{T}}-$$

$$\frac{6.0294}{\tilde{T}^2})\rho+(27.542-\frac{32.898}{\tilde{T}}-\frac{8.7130}{\tilde{T}^2})\rho^2-(8.2606-\frac{12.737}{\tilde{T}}-$$

$$\frac{4.0170}{\tilde{T}^2})\tilde{\rho}^3]\} \qquad (5\text{-}2)$$

Isothermal integration of $\frac{P}{\rho^2}$ from the reference to the final density yields the change in the Hemholtz free energy.

$$\frac{A(\rho,T)-A_o(\rho_o,T)}{RT} = (\frac{\tilde{\rho}_o}{\tilde{\rho}}-1) - \ln\frac{\tilde{\rho}_o}{\tilde{\rho}} - \frac{P_o}{\rho^*RT}(\frac{1}{\tilde{\rho}}-\frac{1}{\tilde{\rho}_o}) + C^*\{(9.8642-$$

$$\frac{10.191}{\tilde{T}}-\frac{1.5356}{\tilde{T}^2})\ln\frac{\tilde{\rho}_o}{\tilde{\rho}}-[(9.8642-\frac{10.191}{\tilde{T}}-\frac{1.5356}{\tilde{T}^2})-(14.2325-$$

$$\frac{15.432}{\tilde{T}}-\frac{3.0147}{\tilde{T}^2})\tilde{\rho}_o+(9.18067-\frac{10.966}{\tilde{T}}-\frac{2.90433}{\tilde{T}^2})\tilde{\rho}_o^2-(2.06515-$$

$$\frac{3.18425}{\tilde{T}}-\frac{1.00425}{\tilde{T}^2})\tilde{\rho}_o^3](\frac{\tilde{\rho}_o}{\tilde{\rho}}-1)+(14.2325-\frac{15.432}{\tilde{T}}-\frac{3.0147}{\tilde{T}^2})(\tilde{\rho}-\tilde{\rho}_o)+$$

$$(4.59033-\frac{5.483}{\tilde{T}}-\frac{1.45217}{\tilde{T}^2})(\tilde{\rho}^2-\tilde{\rho}_o^2)-(0.68838-\frac{1.06142}{\tilde{T}}-\frac{0.33475}{\tilde{T}^2})$$

$$(\tilde{\rho}^3-\tilde{\rho}_o^3)\} \qquad (5\text{-}3)$$

Isobaric temperature differentiation of the pressure yields the thermal pressure coefficient, γ_v.

$$\gamma_v = (\frac{dP_o}{dT}) + (\frac{P-P_o}{T}) - RT(\frac{d\rho_o}{dT}) - \rho^*C^*R\{\frac{1}{\tilde{T}}[(10.191+\frac{3.0712}{\tilde{T}})$$

$$(\tilde{\rho}-\tilde{\rho}_o)-(15.432+\frac{6.0294}{\tilde{T}})(\tilde{\rho}^2-\tilde{\rho}_o^2)+(10.966+\frac{5.80867}{\tilde{T}})(\tilde{\rho}^3-\tilde{\rho}_o^3)$$

$$-(3.18425+\frac{2.0085}{\tilde{T}})(\tilde{\rho}^4-\tilde{\rho}_o^4)] - T[(9.8642-\frac{10.191}{\tilde{T}}-\frac{1.5356}{\tilde{T}^2})$$

$$(\frac{d\tilde{\rho}_o}{d\tilde{T}})-(14.2325-\frac{15.432}{\tilde{T}}-\frac{3.0147}{\tilde{T}^2})(\frac{d\tilde{\rho}_o^2}{d\tilde{T}}) +$$

$$(9.18067-\frac{10.966}{\tilde{T}}-\frac{2.90433}{\tilde{T}^2})(\frac{d\tilde{\rho}_o^3}{d\tilde{T}})-(2.06515-\frac{3.18425}{\tilde{T}}$$

$$\frac{1.00425}{\tilde{T}^2})(\frac{d\tilde{\rho}_o^4}{d\tilde{T}})]\} \qquad (5\text{-}4)$$

where the derivatives of the reference properties P_o and $\tilde{\rho}_o$ are along the path chosen for their variation, usually along saturation line.

The isobaric expansivity α_P then can be calculated through the relation

$$\alpha_P = \kappa_T \gamma_V \tag{5-5}$$

From the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{5-6}$$

The entropy derivative is

$$\left(\frac{\partial S}{\partial \rho}\right)_T = -\frac{\gamma_V}{\rho^2} \tag{5-7}$$

Substitution of Equation (5-4) into Equation (5-7) and isothermal integration from the reference density to the final density yields the entropy change.

$$\frac{S(\rho,T)-S_o(\rho_o,T)}{R} = \frac{1}{R}\left(\frac{1}{\rho}-\frac{1}{\rho_o}\right)\left(\frac{dP_o}{dT}\right) - \tilde{T}\left(\frac{1}{\tilde{\rho}}-\frac{1}{\tilde{\rho}_o}\right)\left(\frac{d\tilde{\rho}_o}{d\tilde{T}}\right) +$$

$$1 - C*\{(9.8642-\frac{20.382}{\tilde{T}}-\frac{4.6068}{\tilde{T}^2})\ln\frac{\tilde{\rho}}{\tilde{\rho}_o}-(14.2325-\frac{30.864}{\tilde{T}}-\frac{9.0441}{\tilde{T}^2})$$

$$(\tilde{\rho}-\tilde{\rho}_o)+(4.59033-\frac{10.966}{\tilde{T}}-\frac{4.3565}{\tilde{T}^2})(\tilde{\rho}^2-\tilde{\rho}_o^2)-(0.68838-\frac{2.12283}{\tilde{T}}$$

$$-\frac{1.00425}{\tilde{T}^2})(\tilde{\rho}^3-\tilde{\rho}_o^3)-\tilde{T}[(9.8642-\frac{10.191}{\tilde{T}}-\frac{1.5356}{\tilde{T}^2})(\frac{d\tilde{\rho}_o}{d\tilde{T}})-(14.2325-$$

$$\frac{15.432}{\tilde{T}}-\frac{3.0147}{\tilde{T}^2})(\frac{d\tilde{\rho}_o^2}{d\tilde{T}})+(9.18067-\frac{10.966}{\tilde{T}}-\frac{2.90433}{\tilde{T}^2})(\frac{d\tilde{\rho}_o^3}{d\tilde{T}}) -$$

$$(2.06515-\frac{3.18425}{\tilde{T}}-\frac{1.00425}{\tilde{T}^2})(\frac{d\tilde{\rho}_o^4}{d\tilde{T}})](\frac{1}{\tilde{\rho}}-\frac{1}{\tilde{\rho}_o})\}+\{1-C*[(9.8642-$$

$$\frac{20.382}{\tilde{T}}-\frac{4.6068}{\tilde{T}^2})-(14.2325-\frac{30.864}{\tilde{T}}-\frac{9.0441}{\tilde{T}^2})\tilde{\rho}_o+(9.18067-\frac{21.932}{\tilde{T}}-$$

$$\frac{8.7130}{\tilde{T}^2})\tilde{\rho}_o^2-(2.06515-\frac{6.3685}{\tilde{T}}-\frac{3.01275}{\tilde{T}^2})\tilde{\rho}_o^3]\}(\frac{\tilde{\rho}_o}{\tilde{\rho}}-1) \tag{5-8}$$

Internal energy U is given by

$$dU = TdS - Pdv \tag{5-9}$$

Isothermal integration and substitution of Equations (5-1) and (5-8) into Equation (5-9) yield the internal energy change.

$$\frac{U(\rho,T)-U_o(\rho_o,T)}{RT} = \frac{1}{R}\left(\frac{1}{\tilde{\rho}}-\frac{1}{\tilde{\rho}_o}\right)\left[\frac{P_o}{T}+\left(\frac{dP_o}{dT}\right)\right] - \tilde{T}\left(\frac{1}{\tilde{\rho}}-\frac{1}{\tilde{\rho}_o}\right)\left(\frac{d\tilde{\rho}_o}{d\tilde{T}}\right) +$$

$$C^*\left\{\frac{1}{\tilde{T}}\left(10.191+\frac{3.0712}{\tilde{T}}\right)\ln\frac{\tilde{\rho}}{\tilde{\rho}_o}-\left(15.432+\frac{6.0294}{\tilde{T}}\right)(\tilde{\rho}-\tilde{\rho}_o)+\left(5.483+\right.\right.$$

$$\left.\frac{2.90433}{\tilde{T}}\right)(\tilde{\rho}^2-\tilde{\rho}_o^2)-\left(1.06142+\frac{0.6695}{\tilde{T}}\right)(\tilde{\rho}^3-\tilde{\rho}_o^3)\Big]+\frac{1}{\tilde{T}}\Big[\left(10.191+\frac{3.0712}{\tilde{T}}\right)$$

$$-\left(15.432+\frac{6.0294}{\tilde{T}}\right)\tilde{\rho}_o+\left(10.966+\frac{5.80867}{\tilde{T}}\right)\tilde{\rho}_o^2-\left(3.18425+\frac{2.0085}{\tilde{T}}\right)\tilde{\rho}_o^3\Big]$$

$$\left(\frac{\tilde{\rho}_o}{\tilde{\rho}}-1\right)+T\Big[\left(9.8642-\frac{10.191}{\tilde{T}}-\frac{1.5356}{\tilde{T}^2}\right)\left(\frac{d\tilde{\rho}_o}{d\tilde{T}}\right)-\left(14.2325-\frac{15.432}{\tilde{T}}-\right.$$

$$\left.\frac{3.0147}{\tilde{T}^2}\right)\left(\frac{d\tilde{\rho}_o^2}{d\tilde{T}}\right)+\left(9.18067-\frac{10.966}{\tilde{T}}-\frac{2.90433}{\tilde{T}^2}\right)\left(\frac{d\tilde{\rho}_o^3}{d\tilde{T}}\right)-\left(2.06515-\right.$$

$$\left.\frac{3.18425}{\tilde{T}}-\frac{1.00425}{\tilde{T}^2}\right)\left(\frac{d\tilde{\rho}_o^4}{d\tilde{T}}\right)\Big]\left(\frac{1}{\tilde{\rho}}-\frac{1}{\tilde{\rho}_o}\right)\Big\} \tag{5-10}$$

The enthalpy H is found from the definition

$$H = U + PV \tag{5-11}$$

Substitution of Equations (5-1) and (5-10) into Equation (5-11) gives the enthalpy,

$$H = U_o(\rho_o,T) + P_o(\frac{2}{\rho}-\frac{1}{\rho_o}) + T(\frac{1}{\rho}-\frac{1}{\rho_o})(\frac{dP_o}{dT}) + RT[(1-\frac{\tilde{\rho}_o}{\tilde{\rho}})-\tilde{T}(\frac{1}{\tilde{\rho}}-\frac{1}{\tilde{\rho}_o})$$

$$(\frac{d\tilde{\rho}_o}{d\tilde{T}}) + C^*RT\{\frac{1}{\tilde{T}}(10.191+\frac{3.2712}{\tilde{T}})\ln\frac{\tilde{\rho}}{\tilde{\rho}_o}+(14.2325-\frac{30.864}{\tilde{T}}-\frac{9.0441}{\tilde{T}^2})$$

$$(\tilde{\rho}-\tilde{\rho}_o)-(9.1807-\frac{16.449}{\tilde{T}}-\frac{5.80863}{\tilde{T}^2})(\tilde{\rho}^2-\tilde{\rho}_o^2)+(2.60515-\frac{4.24567}{\tilde{T}}-$$

$$\frac{1.67375}{\tilde{T}^2})(\tilde{\rho}^3-\tilde{\rho}_o^3)+[(9.8642+\frac{1.5356}{\tilde{T}^2})-(14.2325+\frac{3.0147}{\tilde{T}^2})\tilde{\rho}_o+$$

$$(9.1807+\frac{2.90437}{\tilde{T}^2})\tilde{\rho}_o^2-(2.60515+\frac{1.00425}{\tilde{T}^2})\tilde{\rho}_o^3](\frac{\tilde{\rho}_o}{\tilde{\rho}}-1)+\tilde{T}[(9.8642-$$

$$\frac{10.191}{\tilde{T}}-\frac{1.5356}{\tilde{T}^2})(\frac{d\tilde{\rho}_o}{d\tilde{T}})-(14.2325-\frac{15.432}{\tilde{T}}-\frac{3.0147}{\tilde{T}^2})(\frac{d\tilde{\rho}_o^3}{d\tilde{T}}) +$$

$$(9.18067-\frac{10.966}{\tilde{T}}-\frac{2.90433}{\tilde{T}^2})(\frac{d\tilde{\rho}_o^3}{d\tilde{T}})-(2.06515-\frac{3.18425}{\tilde{T}}-\frac{1.00425}{\tilde{T}^2})$$

$$(\frac{d\tilde{\rho}_o^4}{d\tilde{T}})](\frac{1}{\tilde{\rho}}-\frac{1}{\tilde{\rho}_o})\} \qquad (5\text{-}12)$$

In the above equations, the property value at the state ρ,T can be obtained completely in terms of the property at the state ρ_o,T and, where necessary, derivatives such as $(\frac{d\tilde{\rho}_o}{d\tilde{T}})$ of that state.

Pure Liquid Compression Data Bank

Critical compilations of the experimental data of compressed liquids are scarce. A recent survey of PVT properties of liquids, as referenced in Chemical Abstracts before the end of 1983, was conducted by Tekáč et al.[4] and published in the Journal of Fluid Phase Equilibria in 1985. This survey may serve as a source of references to some original papers on PVT properties of compressed liquids. Our present pure liquid compression data bank contains 133 organic and inorganic liquids (including liquefied gases and metallic liquids), 13 molten salts, 17 polymer melts, and 7 deuteriated liquids. They are listed separately in the first column from Table 5-1 to Table 5-4. The substance order is based on the Chemical Abstracts system. In the case where the substance has been studied by several authors or by the same author with several investigations, the reference numbers are ordered chronologically. Only those data sets with the pressure ranges greater than 300 bar and temperatures more than two isotherms have been selected. There are 234 total data sets. Several misprints have been found in the printed values of the experimental data in the original articles. They have been corrected in the present data bank.

Experimental determination of the volumetric properties of compressed liquids may be divided into two methods: direct measurements and indirect measurements. The major sources of the experimental data in the present

data bank come from the direct measurements of volume change or volume itself as a function of pressure at constant temperature such as from piezometric[68] or pycnometric methods.[69] Isochoric data[70] are generally not included in the data bank because they are not available in isothermal form. Only a small portion comes from the indirect methods where liquid density can be related to the other physical properties such as ultrasonic velocity, dielectric constant, refractive index, and heat capacity, etc. In the case of the ultrasonic velocity measurement,

$$\kappa_T = \frac{1}{\rho u^2} + \frac{T\alpha_P^2}{\rho C_P} \qquad (5\text{-}13)$$

where u is the velocity of sound. Isothermal integration from the reference pressure P_o to the final pressure P yields the density expression.[71]

$$\rho = \rho_o + \int_{P_o}^{P} \frac{1}{u^2} dP + T \int_{P_o}^{P} \frac{\alpha_P^2}{C_P} dP \qquad (5\text{-}14)$$

In the case of the dielectric constant measurements, the theoretical expression of the Clausius-Mossotti Equation[29] can be written as

$$\rho = \frac{1}{CM} \frac{\varepsilon - 1}{\varepsilon + 2} \qquad (5\text{-}15)$$

where CM is the Clausius-Mossotti function[72-74] and ε is the dielectric constant. Similarly, for infractive index measurements the Lorentz-Lorenz Equation[25] can be written as

$$\rho = \frac{1}{LL} \frac{n^2-1}{n^2+2} \tag{5-16}$$

where LL is the Lorentz-Lorenz analogue[74] of the Clausius-Mossotti function CM which replaces ε in Equation (5-15) with n^2, the square of the refractive index.

The direct measurements tend to be more accurate than the indirect measurements. The accuracy of the experimental data varies from 0.01% to 1% in density. Generally, a precision of 0.1% in density corresponds to 1% in pressure or 1-10% in isothermal compressibility.

Results and Discussions

The pressure Equation (5-1) can be used as an equation of state for pure liquids. If the characteristic parameters are known for a specific substance, then the change in pressure due to an isothermal change in density can be calculated. On the other hand, Equation (5-1) can also be used as a correlation scheme to fit the liquid compression data. Tables 5-1 to 5-4 list the characteristic parameters for all of the substances in the present data bank. The results are in excellent agreement with the experimental data for all of the substances over all data ranges. In

Table 5-1

Characteristic Parameters and Comparisons with Liquid Compression Data

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
Argon	17.7363	28.6692	145.647	0.9052	48	90-140	22.4-2497	36
	16.5475	28.8229	150.113	0.5093	154	110-147	12.5-1422	75,76
Bismuth	18.2663	27.7070	751.293	1.1289	9	550-950	0-8000	77
Dichlorodifluoromethane	37.3342	75.9700	373.366	1.4629	38	253-313	1.52-1608	78
Trichlorofluoromethane	30.7966	89.4542	455.306	0.4633	16	341-460	107-1594	79
Carbon tetrachloride	41.9381	95.6553	489.902	0.2141	24	298-358	0-1000	66
	42.0350	95.5192	488.580	1.5006	25	273-323	1-1977	80
	44.3621	95.0146	507.552	0.9514	44	313-373	1.01-2622	81
Carbon monoxide	20.7868	34.1649	125.638	0.9061	72	82-125	19.8-1397	82
Carbon disulfide	29.0507	59.6196	424.798	1.1426	44	223-298	1-2028	80
Chlorodifluoromethane	24.8969	59.9348	356.229	1.5669	38	253-313	2.43-1596	78

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
Trichloro-methane	54.7671	75.3199	414.111	0.9860	14	303-363	30-4000	83
	36.9601	79.1835	468.398	0.6586	32	273-348	0.1-987	84
Dichloro-methane	250.711	44.2208	281.633	3.6907	20	303-323	1.01-5189	85
	26.3340	64.0808	462.224	0.8314	24	298-348	0.6-1013	84
Methyl bromide	21.6065	54.5703	443.891	1.0955	36	253-313	0.4-1595	78
Chloromethane	25.5235	48.1691	366.157	0.7966	36	253-313	1.22-1595	78
Methyl iodide	26.6306	62.4797	433.610	1.7119	20	273-363	1-2500	86
	29.2767	61.0318	465.803	0.6581	36	253-313	0.1-1595	78
Methane	14.7376	38.7225	190.711	0.1452	80	95-185	0.65-4785	44
	20.2269	37.1619	182.236	1.3459	19	105-160	0.57-2094	87
	17.2607	37.9177	180.204	0.7636	109	110-147	10-1281	88,89
Methanol	15.9908	39.5268	506.620	1.5166	32	323-473	134-1392	90
	23.8523	37.6472	420.711	1.9036	61	283-348	1-2075	91
	16.4759	39.5920	492.130	1.1207	80	298-473	0.17-1000	67
	22.6415	37.8518	420.349	0.8369	35	278-323	1-2750	92
Acetonitrile	20.2608	51.8140	438.583	1.0996	21	303-393	30-4500	93
Ethylene	23.9617	47.9370	265.921	0.7727	43	160-250	5-1300	59

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	P,bar	Ref.
1,1-Dichloro-ethane	28.2808	84.8104	488.322	0.9888	40	298-398	0.3-1013	94
1,2-Dichloro-ethane	30.4401	82.0062	517.867	0.8907	40	298-398	0.1-1013	94
Acetic acid	32.8191	55.7849	493.835	0.3249	18	298-328	1.01-2533	95
Ethyl bromide	27.7857	73.3477	474.360	1.3446	36	253-313	0.1-1568	78
Ethane	25.1652	53.6389	293.737	1.0062	64	140-280	0.6-745	60
Ethanol	19.3553	59.2663	538.568	2.3471	15	293-353	0-4903	96
	38.1417	54.5444	415.781	1.3305	46	298-323	1-3104	97
	22.3241	58.0450	486.624	1.4371	43	298-348	1-1962	50
Dimethyl sulfoxide	61.5869	70.0619	442.503	2.1925	31	294-323	0-1500	98
Ethylene glycol	33.9809	59.6111	603.269	0.3862	24	298-358	0-1000	66
Ethylene carbonate	68.3229	65.2805	646.152	1.4247	14	353-393	1-1400	99
Propylene	23.6708	67.5402	355.272	1.5945	65	273-353	19.6-1029	100
Acetone	35.0617	72.3087	566.224	1.3519	49	298-398	10.1-4119	101
Methyl acetate	63.4474	72.7310	428.005	1.3335	36	253-313	0-1568	78

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
Propionic acid	39.1760	73.5143	515.340	0.2189	18	298-328	1.01-2533	95
Propane	29.2700	72.0274	345.560	0.5484	56	200-320	0.2-712	61
Isopropanol	26.8345	78.6194	750.459	1.3412	60	298-398	10.1-4119	101
Glycerol	71.1156	76.3347	736.593	1.3414	38	323-523	135-1477	90
Perfluorocyclobutane	39.4863	114.173	389.817	1.2250	20	323-373	50-1740	102
Furan	49.1557	67.7580	428.410	1.2001	169	225-257	1-8830	103
Vinyl acetate	35.4288	91.0150	421.669	0.5092	55	298-398	10.1-3923	101
n-Butyraldehyde	41.7832	90.3996	552.808	2.4365	36	303-333	1.01-2765	104
Methyl ethyl ketone	67.0723	82.3974	420.479	5.2120	18	303-343	0-1720	105
Tetrahydrofuran	197.721	63.5865	299.328	3.3331	14	303-323	1.01-5170	85
Ethyl acetate	146.386	79.7130	305.153	2.7803	14	303-323	1.01-5127	85
	*54.8846	93.1047	460.697	1.2965	36	253-313	0-1568	78
Isobutyric acid	53.3627	90.2104	520.614	0.5695	18	298-328	1.01-2533	95
n-Butane	32.3974	90.6076	396.630	0.5258	32	240-360	0.24-714	62
Isobutane	30.7976	92.2552	383.286	0.5606	32	240-360	0.4-711	63
Diethyl ether	51.5640	95.1122	377.696	1.8304	70	293-353	1.01-12159	96

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°K	AAE,%	No. of Points	Data Range T,°k	P,bar	Ref.
t-Butanol	60.8345	88.4142	464.922	0.5197	39	323-423	0-8000	90
Tetramethyl-silane	52.4182	122.908	405.826	1.0866	40	298-373	45-4500	35
	52.8151	122.752	402.484	1.0729	41	298-373	46-4500	106
Tetramethyl-tin	54.9820	132.278	527.717	1.1879	22	258-398	1-4000	107
Pyridine	36.0670	83.7184	571.697	1.4617	43	303-423	1-4000	108
Cyclopentane	26.9889	95.5073	530.684	0.1859	24	298-353	0.98-1961	109
i-Pentene	24.3908	108.467	453.659	0.9398	38	353-448	5.7-316	110
Neopentane	35.9999	112.318	415.085	0.7855	16	348-373	6.75-316	111
Isopentane	47.7900	106.289	432.174	0.7293	41	223-298	1-2028	80
n-Pentane	7.48978	135.279	628.365	4.3400	25	311-361	1.08-690	112
Perfluorobenzene	77.7432	106.765	440.043	2.9766	42	288-423	1-2500	113
	75.3355	108.077	465.700	0.5286	22	298-373	1-3104	114
Bromobenzene	42.2245	110.530	568.512	0.2348	24	298-358	0-1000	47
Chlorobenzene	*40.3277	105.940	551.255	0.2155	24	298-358	0-1000	47
	40.2752	109.467	399.994	1.5115	11	303-323	1.01-5096	85
Nitrobenzene	*48.2536	109.179	586.729	0.3169	24	298-358	0-1000	47
	68.0672	105.079	491.797	0.4617	28	293-313	1-1000	115

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
Benzene	38.0877	89.2371	497.400	0.3839	24	298-358	0-1000	47
	47.4353	87.6248	487.163	0.9113	33	303-433	1-4544	35
	47.3037	87.6609	487.028	0.9445	32	303-433	1-4000	106
	35.6040	89.8287	502.920	0.1804	18	293-313	1-1289	116
	*57.4441	85.1985	473.577	0.5561	43	298-348	1-1051	117
	54.2541	85.5564	453.078	0.9287	30	298-373	1-3914	114
	54.9147	85.5176	457.325	0.1244	24	288-313	1-350	118
Aniline	48.2882	96.8373	576.030	0.2326	24	298-358	0-1000	47
Cyclohexane	*34.9788	110.347	536.969	1.0726	49	344-511	53.5-677	119
	34.2241	111.266	513.297	0.1873	9	313-353	0.98-1177	109
	*44.5619	107.881	539.727	0.2195	8	298-348	1-1000	120
	52.4305	105.450	493.310	0.9742	35	298-348	1-1053	117
	*43.0528	108.490	558.646	1.6164	42	313-383	1-2140	121
	54.0977	105.252	501.965	2.7124	33	287-338	1-1100	122
	48.5859	106.335	514.633	0.3733	24	288-313	1-350	118
Methylcyclopentane	46.4833	110.127	507.509	1.7919	41	298-348	1-1962	50
2,2-Dimethylbutane	24.0891	135.192	480.776	2.3827	69	373-473	10.1-304	123

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	P,bar	Ref.
n-Hexane	*23.1691	136.583	498.619	1.7140	43	373-498	5.67-316	124
	71.9438	119.539	424.813	0.5782	44	273-333	1.01-5066	125
	60.8798	122.219	453.699	0.4880	24	273-333	0-5018	64
	53.0649	123.896	423.590	0.2909	24	298-353	0.98-1961	109
	74.4525	119.114	423.637	0.8048	31	298-373	1-5640	126
	*67.0976	120.896	449.005	1.7835	18	298-348	1-5000	120
2-Methylpentane	28.6649	132.906	480.616	1.2660	37	373-473	5.66-316	124
3-Methylpentane	32.2747	130.184	488.963	2.3598	47	348-473	5.67-316	110
Isopropyl ether	73.4113	128.570	367.933	2.1644	14	303-323	1.01-5113	85
Toluene	59.2518	104.145	479.754	1.1031	43	223-298	1-2028	80
	45.5918	107.629	574.807	0.4805	30	293-313	1-2000	116
Anisole	53.9271	112.126	535.928	0.5358	24	298-353	0.98-1961	109
Cycloheptane	49.6542	123.283	533.605	0.6745	16	298-353	0.98-1961	109
Methycyclohexane	73.9784	122.249	478.370	1.5786	30	203-298	1-5000	127
3-Ethylpentane	58.9151	139.668	489.463	0.3305	24	298-353	0.98-1961	109

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
n-Heptane	84.1373	135.399	433.293	0.5074	44	273-333	1.01-5066	125
	49.8654	144.694	521.251	1.8289	72	311-511	60-691	128
	64.3441	140.665	462.152	1.5689	34	273-393	0-1177	129
	49.8654	144.694	521.251	0.9351	40	303-473	0-5000	130
	50.8954	144.512	499.512	0.2749	24	298-353	0.98-1961	109
	52.4577	143.682	493.186	1.8294	45	298-348	1-1962	50
2,2,3-Trimethyl-butane	45.5561	140.797	524.835	0.4893	15	298-353	0.98-1569	109
o-Xylene	33.4430	128.981	656.224	0.4682	19	293-313	1-2000	116
n-Octane	43.4517	163.870	518.991	3.9254	56	373-523	5.07-304	123
	87.9996	154.689	462.599	0.5436	39	273-333	1.01-5066	125
	57.2025	162.127	508.535	0.6614	28	303-393	0-1177	129
	82.9251	155.088	462.530	1.5882	28	298-348	1-4795	131
Hexamethylethane	50.6789	158.191	532.879	2.5329	38	393-543	10.1-304	132
2,2,4-Trimethyl-pentane	32.7867	171.242	528.894	0.6635	46	373-523	5.07-304	123
	91.9651	153.133	473.690	0.8582	47	298-373	1-5389	133

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
Octamethylcyclo-tetrasiloxane	143.728	295.684	489.515	0.8358	28	313-373	1.01-1662	81
3,3-Diethylpentane	68.3054	171.636	625.689	1.1587	31	303-423	0-8000	43
n-Nonane	70.7412	178.153	547.242	0.3318	28	303-393	0-1177	129
	56.6153	181.817	587.459	0.8950	40	303-523	0-5000	130
	70.7588	177.199	536.600	0.6852	34	303-423	0-6000	43
trans-Decalin	64.4222	165.611	588.268	0.7836	24	298-353	0.98-1961	109
n-Decane	95.9055	190.643	498.819	1.0601	19	298-373	1-4202	131
	102.460	189.488	532.570	1.9948	32	298-358	1.01-5171	65
n-Decanol	42.0686	216.366	680.358	3.0555	26	298-353	0-1373	134
Isodecanol	51.9110	208.538	786.533	1.8039	44	298-353	0-1961	134
n-Undecane	66.5577	217.978	615.740	1.1974	48	303-523	0-5000	130
Crown ether	113.901	242.730	767.519	1.0210	32	373-523	142-1547	90
n-Dodecane	231.541	207.772	488.844	1.9995	78	311-408	1.01-6891	135
	95.0230	230.069	583.176	0.3470	24	303-393	0-1177	129
	101.328	227.886	575.898	1.5527	32	298-358	1.01-4137	65
	91.4995	230.699	607.689	3.0083	96	298-358	1.01-4169	65
	106.101	226.146	542.992	1.0108	34	298-373	1-4419	131

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
4,4-Dipropyl-heptane	90.2694	243.422	637.160	0.6208	30	303-373	0-5000	43
n-Tridecane	73.7403	255.137	654.379	1.3647	48	303-523	0-5000	130
1,1-Dephenyl-ethane	100.605	189.535	627.060	0.3984	30	311-372	1.01-3400	136
n-Tetradecane	119.758	261.484	563.229	2.3681	117	298-358	1.01-3668	65
1-Methoxyphenyl-1-Phenyl-ethane	92.2505	217.670	669.302	0.7435	24	298-353	0.98-1961	109
1-Methoxycyclo-hexyl-1-Cyclo-hexylethane	99.1289	255.878	633.814	0.6137	24	298-353	0.98-1961	109
n-Pentadecane	179.006	269.053	554.691	1.4937	69	311-408	1.01-6546	135
n-Hexadecane	135.480	297.194	595.105	0.4203	24	303-393	0-1177	129
	134.131	295.995	567.607	1.2604	26	298-358	1.01-2757	65
	105.988	304.393	617.277	3.1369	73	318-358	1.01-2902	65
	120.028	299.559	602.368	0.5354	23	298-373	1-4505	126

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
5,5-Dibutyl-nonane	123.093	310.847	657.741	1.1984	31	303-433	0-8000	43
n-Heptadecane	88.1203	329.801	706.134	1.2868	48	323-573	0-5000	130
	120.280	318.556	627.446	0.6331	29	333-453	0-8000	43
1,2,3,4,5,6,7,8,13,14,15,16-Dodecahydrochrysene	125.191	244.067	751.127	1.4455	4	311-408	1.01-3400	136
Perhydrochrysene	109.013	270.042	783.426	1.4653	54	311-408	1.01-3400	136
n-Octadecane	187.659	323.130	588.922	0.9911	53	333-408	1.01-5513	135
1,1-Diphenyl-heptane	123.163	278.667	683.275	1.3626	41	311-408	1.01-3400	136
7,n-Hexyltri-decane	136.211	359.715	625.887	0.8747	40	311-408	1.01-3400	136
n-Eicosane	98.0865	386.335	737.725	1.3859	40	373-573	0-5000	130
Bixylyltoluene	144.750	296.618	612.170	0.1874	24	298-353	0.98-1961	109

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
Bicyclohexyl-toluene	160.457	352.058	606.071	0.3060	24	298-353	0.98-1961	109
2,4-Bis-(α-phenylethyl)-phenylmethylether	112.682	326.812	728.355	0.3975	24	298-353	0.98-1961	109
2,4-Bis-α-cyclohexylethyl)-cyclohexylmethyl-ether	116.082	378.016	683.115	0.5837	24	298-353	0.98-1961	109
1-phenyl-3(2-phenyl-ethyl) hendecane	117.564	398.589	739.649	1.0506	135	311-408	1.01-8958	135
1-α-Naphtayl-pentadecane	266.794	372.792	615.362	1.0329	48	333-408	1.01-5513	135
9(2-phenylethyl) heptadecane	233.172	408.388	618.091	1.1503	132	311-408	1.01-9647	135
1,7-Dicyclopentyl-4 (3-cyclopentylpropyl) heptane	200.999	403.698	660.418	1.1609	119	311-408	1.01-10337	135

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
1-cyclohexyl-3(2-cyclohexyl-ethyl) hendecane	179.644	422.795	662.385	1.0291	109	311-408	1.01-8958	135
1-cyclopentyl-4(3-cyclopentylpropyl) dodecane	233.201	413.155	596.681	1.6144	155	311-408	1.01-10337	135
1-α-Decalyl-pentadecane	221.510	414.182	674.410	0.7107	54	333-408	1.01-5857	135
9(2-Cyclohexylethyl) heptadecane	227.263	428.837	638.810	0.9820	133	311-408	1.01-10337	135
9(3-Cyclopentylpropyl) heptadecane	222.792	430.734	619.719	1.0514	145	311-408	1.01-10337	135
9-n-Octylhepta-decane	228.384	444.701	599.505	1.2509	146	311-408	1.01-10337	135

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	Data Range P,bar	Ref.
1,1-Diphenyl-tetradecane	183.555	398.592	688.199	2.0528	31	333-408	1.01-3400	136
Squalene	258.312	491.140	559.716	0.6349	24	298-353	0.98-1961	109
Squalane	223.451	541.486	594.137	0.6172	24	298-353	0.98-1961	109
n-Triacontane	140.659	570.480	783.517	1.6095	40	373-573	0-5000	130
1,1-Di(α-decalyl)-hendecane	276.663	474.895	676.267	1.5014	41	311-408	1.01-3000	136
11-n-Decylhenei-cosane	275.270	539-584	613.412	0.9488	33	311-408	1.01-3400	136
13-n-Dodecylhexa-cosane	285.514	664.015	637-798	0.8561	35	311-408	1.01-3400	136
n-Tetracontane	203.694	745.195	780.353	2.1338	32	423-573	0-5000	130

Table 5-1 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	P,bar	Ref.
Water	15.6558	17.9402	326.221	0.8070	24	298-358	0-1000	66
	6.80856	32.0515	604.809	7.5498	18	303-343	0-1720	105
	19.7417	17.3482	427.493	2.4946	40	273-373	0-1000	137
	15.8098	17.8588	318.117	1.6205	58	283-348	1-2077	91
	7.49609	20.1175	424.182	0.9470	42	348-573	0.39-10000	45
Ammonia	12.2033	26.0062	380.914	1.7643	41	253-313	1.97-1797	138
Mercury	27.0455	17.5290	848.180	0.4784	56	303-423	0-8000	139
Krypton	15.6019	35.4823	207.290	0.4752	34	120-200	5.07-3040	56
	16.3006	35.1179	199.391	0.4546	60	129-147	10.4-1147	76
Nitrogen	16.7950	34.7248	124.803	0.8033	29	77-122	8.64-519.4	58
	17.3745	34.4744	124.388	0.8252	32	110-120	19-1377	88
Oxgen	20.3573	27.6646	147.217	0.4277	17	90-118	7.92-504.3	58
Sulphur Dioxide	9.04891	48.4053	444.752	2.0502	37	323-423	8.6-318.5	140
Xenon	16.3046	45.4322	279.633	0.3132	36	170-260	5.07-2533	57

Table 5-2

Characteristic Parameters and Comparisons with Molten Salt Compression Data

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	P,bar	Ref.
Potassium chloride	16.9363	20.5829	1526.36	1.0932	43	1073.15-132-3.15	1-6000	141
Potassium nitrate	14.1174	63.7239	1208.28	2.0503	20	673.15-773.15	0-9119.25	142
Rubidium nitrate	76.0519	57.0353	666.713	1.0963	15	673.15-773.15	0-9119.25	142
Silver nitrate	63.3071	44.5619	942.390	0.5432	20	573.15-773.15	0-9119.25	142
Tetrapropyl-phosphonium tetrafluoro-borate	154.376	285.130	789.574	0.7171	16	520.94-530.80	1.01-1725.80	143
Tetrapropyl-arsonium tetrafluoro-borate	545.175	243.825	567.151	1.8690	24	503.55-512.75	1.01-2503.55	143
Tetrabutyl-ammonium tetrafluoro-borate	165.853	346.826	947.901	0.3511	39	420.15-480.15	10-1000	144

Table 5-2 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	P,bar	Ref.
Tetrapentyl-ammonium tetrafluoro-borate	161.310	423.485	924.715	0.5654	56	402.88-494.51	10-2000	144
Tetrahexyl-ammonium tetrafluoro-borate	231.879	484.140	808.913	0.1484	42	394.15-473.15	10-2000	144
Tetraheptyl-ammonium tetrafluoro-borate	239.349	561.309	886.090	0.3640	54	407.15-503.15	10-2000	144
Tetraethyl-ammonium tetrapropyl-borate	86.3565	201.036	733.253	0.1562	39	363.15-403.15	0-4200	48

Table 5-2 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	P,bar	Ref.
Tetrapropyl-ammonium tetraethyl-borate	66.3607	205.720	849.931	0.4424	16	393.15-433.15	0-1400	48
Tetrabutyl-ammonium tetrabutyl borate	128.281	303.900	757.227	0.1661	20	393.15-433.15	0-5000	48

Table 5-3

Characteristic Parameters and Comparisons with Polymeric Liquid Compression Data

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	P,bar	Ref.
Poly(tetrafluo-ethylene)	150.116	5.09707	669.489	1.9100	19	615.95-645.55	0-392.27	145
Poly(vinyl chloride)	64.6474	0.85999	1896.22	0.4133	17	355.15-370.15	0.98-1373.91	146
Low Density Polyethylene	106.473	1.43576	1289.71	0.9439	38	423.55-476.15	0.98-1962.31	146
High Density Polyethylene	394.030	1.27585	744.323	1.0049	32	402.95-447.65	0.98-1962.31	146
Branched Polyethylene	356.322	1.28835	798.313	0.9673	78	398.25-471.15	1-2000	147
Linear Polyethylene	550.584	1.21975	685.795	0.8014	67	415.25-472.85	1-2000	147
High Molecular Weight Linear Polyethylene	773.266	1.18514	617.496	0.7953	60	409.85-472.65	1-2000	147

Table 5-3 (Continued)

Substance	-C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T,°k	P,bar	Ref.
Silicone Oil Bayer M 100	312.579	1.05217	555.488	0.3991	24	298.15-353.15	0.98-1961.33	109
Silicone Oil Bayer M 1000	396.912	1.02254	522.659	0.3299	24	298.15-353.15	0.98-1961.33	109
cis-1,4-Poly-butadiene	628.687	1.15168	538.466	0.9608	128	277.15-317.65	1.01-2786.44	148
Poly(methyl methacrylate)	232.062	0.94655	962.326	0.3804	41	386.65-432.15	1-2000	147
Poly(4-methyl-pentene-1)	379.695	1.27596	787.879	1.3781	126	513.65-592.05	0-1961.33	145
Polystyrene	222.252	1.07308	1054.65	1.7755	73	388.55-522.05	0.98-1766.18	146
	273.239	1.05128	955.103	1.5730	69	388.55-468.75	1-2000	149
Poly(n-butyl methacrylate)	288.719	1.05218	817.028	0.8120	167	307.05-472.65	1-2000	147
Poly(orthomethyl-styrene)	215.627	1.09430	1207.95	1.2974	50	412.55-470.85	1-1800	149
Poly(cyclohexyl methacrylate)	131.047	1.06464	1173.20	0.8374	89	395.85-472.05	1-2000	147

Table 5-4

Characteristic Parameters and Comparisons with Deuteriated Liquid Compression Data

Substance	C*	V*,cc/mol	T*,°k	AAE,%	No. of Points	Data Range T°k	Data Range P,bar	Ref.
Chloroform-d	61.0950	74.8436	406.254	0.7269	17	303-363	30-4500	83
Methanol-d	18.6288	38.8181	414.399	0.9990	38	243-323	15-4905	150
Acetonitrile-d_3	19.6590	52.0451	449.167	0.8564	15	303-363	30-4000	93
Fluorobenzene-d_5	50.8996	97.3255	472.832	0.9066	11	303-373	1-2000	151
	36.5382	101.294	569.539	1.0932	33	303-423	60-3500	152
Benzene-d_6	44.5191	88.5889	472.057	1.3727	18	303-393	50-4000	153
	53.2186	85.5476	466.009	1.2636	34	324-374	1-4032	114
	63.7417	84.0675	448.796	0.2365	24	288-313	1-350	118
Cyclohexane-d_{12}	37.8479	109.170	574.821	0.7602	24	288-313	1-350	118
Tolune-d_8	70.6727	102.623	486.850	1.5641	38	238-473	1-4000	154

fact, they all appear to be within experimental error. This proves the generality and flexibility of the present correlation. The characteristic parameters for each substance evaluated from the liquid compression data with those from the liquid DCFI data are very close to each other except for the data of Grindley.[43] This discrepancy is probably due to the experimental uncertainty of liquid DCFI at low pressure where Grindley's mathematical treatment of the compression data is questionable. The general similarity of the characteristic parameters for each substance indicates the thermodynamic consistency of the present approach. Both the compressibility Equation (4-1) and the pressure Equation (5-1) with the same parameters reproduce the crossover behavior of the volumetric properties of compressed liquids discussed in Chapter 3.

The characteristic parameters are optimized only in the tabulated data ranges. Thus computations performed outside the data ranges for some substances may be less accurate. This is especially true for those highly polar and associating species where the characteristic parameters are evaluated from a very narrow data ranges or from questionable data sets such as the case of Schornack and Eckert.[85] The characteristic parameters are evaluated from two isotherms with a temperature span of 20°K and the experimental accuracy in density of 0.3% only. Though the fitted results are within the experimental errors (less than 3% in pressure), the characteristic parameters are

probably not as reliable as those from the more accurate experimental results. Even so, extrapolations from the present correlation should be more reliable than from other correlations. This is particularly important in physical properties correlation since experimental data covering the whole state conditions are not always available.

There are a number of substances where several sets of characteristic parameters are tabulated together because several sets of measurements exist. For a substance with similar parameter sets, in most cases, any one set can be used as the characteristic parameter set. This is the case for most of the normal liquids where the characteristic parameters are found over a wide range of state conditions. For substances with different parameter sets, the recommended values are characterized with an asterisk. Variations of the characteristic parameters are due mainly to the precision of the experimental results and the insensitivity of the DCFI and pressure changes to parameter variations. It may be that some sets are not equivalent because of limited ranges of measurement as for some polar and associating substances. The recommended characteristic parameters are based on the data range, experimental precision, and accuracy of the measurements. There is a preference in this work for the data of some authors. Generally, they are liquefied noble gases and others from Streett and his coworkers,[56,57] liquefied natural and petroleum gases from the National

Bureau of Standards (NBS),[60-63] hydrocarbons from Dymond et al.,[126,131,133] long chain hydrocarbons from Doolittle,[130] coal liquids (PSU compounds) from Cutler, et al.[135] and Lewitz et al.,[136] benzene and its derivatives from Gibson and Loeffler,[47,66] cyclic compounds from Kuss and Taslimi,[109] polar liquids from Kumagai and his coworkers,[78,84,138] alcoholic liquids from Makita and his coworkers,[91,97] liquid acids from Karpela,[95] molten salts from Barton and Speedy,[144] polymer melts from Simha and his coworkers,[147,149] and deuteriated liquids from Jonas and his coworkers[83,93,150-154]

Group Contribution Method

In addition to the molecular corresponding states correlations of the above type, group contribution methods are very useful for physical property estimation. The concept assumes that each molecule is made up of different types of atomic or structural groups and that the molecular properties can be evaluated from contributions of these atomic or structural groups. Unlike the corresponding states correlation, the fundamental assumption is that various groups in a molecule contribute a definite value to the total properties independent of the presence of the other groups on the molecule.[155]

There are two general approaches in group contribution method. The first one may be called the property-additive approach. It assumes that the groups actually

posses thermodynamic properties or make directly additive contributions to the molecular properties.[156] The molecular properties then can be calculated from the sum of these group properties.

$$M_i = \sum_{\alpha} \nu_{i\alpha} M_{\alpha} \qquad (5\text{-}17)$$

where $\nu_{i\alpha}$ is the stoichiometric coefficient, represents the number of groups or type α in molecule i. This approach has been applied to the liquid molar volume at the normal boiling point[157] and to the liquid heat capacity,[158] as well as to the solution of group methods for activity coefficient.[159,160] This group contribution method has also been widely used for ideal gas properties such as heat capacity, entropy, and enthalpy of formations[155] etc., where intra- or intermolecular forces play no role. For the DCFI, Equation (5-17) would yield

$$C_i = \sum_{\alpha} \nu_{i\alpha} C_{\alpha} \qquad (5\text{-}18)$$

The other general group contribution method may be called the parameter-additive approach. It assumes that the molecular property can be written as a function of the state variables, $\underline{x}$, and a set of parameters, $\underline{\theta}$.

$$M_i = f(\underline{x};\underline{\theta}) \qquad (5\text{-}19)$$

where

$$\theta_i = \sum_\alpha \nu_{i\alpha}\, \theta_\alpha \qquad (5\text{-}20)$$

This approach has been applied to the estimation of the critical properties by Lydersen.[155]

Evaluation of the molecular parameters from Tables 5-1 to 5-4 shows that these parameters appear to be group additive, according to Equation (5-20). Thus, the DCFI can be written as

$$C_i = C_i^* f(\rho V_i^*, T^*/T) \qquad (5\text{-}21)$$

and

$$V_i^* = \sum_\alpha \nu_{i\alpha} V_\alpha^* \qquad (5\text{-}22)$$

$$C_i^* = \sum_\alpha \nu_{i\alpha} C_\alpha^* \qquad (5\text{-}23)$$

Table 5-5 lists the group parameters that can be added for each group to estimate the crossover parameters for some of the substances. By adopting $T^*=0.96T_c$, comparisons of the group contribution correlation with liquid n-alkane compression data are listed in Table 5-6. The results are satisfactory.

Table 5-5

Group Contributions to Characteristic Parameters C* and V*

Group (Attachment)	-C*(±0.5)	V*, cm^3/mol(±0.05)
$-CH_3$ (Linear paraffin)	12.6	26.83
$-CH_3$ (nonlinear paraffin)	9.7	26.02
$-CH_2-$ (linear paraffin)	4.3	18.35
$-CH_2-$ (nonlinear paraffin)	7.9	16.54
$-CH_2-$ (ring)	5.8	18.39
-CH< (nonring)	2.3	12.20
-CH< (aromatic ring)	6.8	14.77
>C<	-3.4	9.95
>Si< (silicon)	11.9	17.72
>Sn< (tin)	16.4	28.20
-F (on nonring)	6.7	12.40
-Cl (on nonring)	12.5	21.29
-Br (on nonring)	9.1	28.23
-COOH (on nonring)	21.2	28.64
-COO- (ester on nonring)	25.0	21.10

Table 5-6

Group Contribution Correlation and Comparisons with n-Alkane Liquid Compression Data

Substance	Data Range T*, °k	Data Range P, bar	No. of Points	AAE%	Ref.
Ethane	140-280	0.6-745	64	1.1396	60*
Propane	200-320	0.2-712	56	2.8171	61*
n-Butane	240-360	0.2-714	32	2.7298	62*
n-Hexane	373-498	5.7-316	43	8.3906	124
	273-333	1.01-5066	44	4.5357	125
	273-333	0-5018	24	4.7963	64
	298-353	0.98-1961	24	5.1995	109
	298-373	1-5640	31	7.9198	126
	298-348	1-5000	18	6.1217	120
n-Heptane	273-333	1.01-5066	44	2.2857	125
	311-511	60-691	72	1.4267	128
	273-393	0-1177	34	7.1420	129
	303-473	0-5000	40	1.8006	130*
	298-353	0.98-1961	24	3.6664	109
	298-348	1-1962	45	3.4231	50
n-Octane	273-333	1.01-5066	39	6.1787	125
	303-393	0-1177	28	4.8369	129
	298-348	1-4795	28	3.5022	131

Table 5-6 (Continued)

Substance	Data Range T*,°k	Data Range P,bar	No. of Points	AAE%	Ref.
n-Nonane	303-393	0-1177	28	5.2361	129
	303-523	0-5000	40	1.1937	130*
	303-423	0-6000	34	2.7034	43
n-Decane	298-373	1-4202	19	5.8403	131
	298-358	1.01-5171	32	5.8503	65
n-Undecane	303-523	0-5000	48	1.2400	130*
n-Dodecane	303-393	0-1177	24	5.4369	129
	298-358	1.01-4169	96	5.0177	65
	298-373	1-4419	34	2.9645	131
n-Tridecane	303-523	0-5000	48	1.3080	130*
n-Tetradecane	298-358	1.01-3668	111	3.0158	65
n-Pentadecane	311-408	1.01-6546	69	9.2190	135
n-Hexadecane	303-393	0-1177	24	6.0542	129
	298-358	1.01-2757	26	3.0534	65
	298-373	1-4505	23	1.6549	126
n-Heptadecane	323-573	0-5000	48	1.2701	130*
	333-453	0-8000	29	2.2816	43
n-Octadecane	333-408	1.01-5513	53	6.1837	135
n-Eicosane	373-573	0-5000	40	1.5952	130*

*Group parameters are estimated from these data sets

CHAPTER 6
APPLICATION OF THE MODEL TO LIQUID MIXTURES

Introduction

Mixtures of compressed liquids are the most prevalent form of material found in high pressure chemical processes such as hydrogenation, polymerization, and some other energy-related processes as well as geological systems, including oil and steam reservoirs, for example, the syntheses of ammonia and methanol, petrochemical or coal hydrogenation, the fabrication of polyethylene, etc. Despite their technological importance, the state of knowledge about their compositional and density dependence of the thermodynamic properties of compressed liquid mixtures is still not known in enough detail to be applicable to process calculations. Though there exists a rigorous formula for the reduced bulk modulus of a mixture in terms of the quadratic mole fraction average of the binary DCFI,[24] the present model of Equation (4-1) does not provide a means for obtaining the unlike pair DCFI. An expedient alternative is to use a one-fluid concept[161] to obtain the mixture characteristic parameters as a function of composition and the pure component characteristic parameters. The pressure equation with mixing rules for the

parameters has been applied to all of the compression data in the present compressed liquid mixture data bank. The results with and without a binary parameter are tabulated. For mixtures with negligible excess volume, the simple (mole fraction average) mixing rules work as well for mixtures as does the fitting of the pure components.[162] This is consistent with the findings of the parameter-additive group contribution described in the last chapter.

Derived Thermodynamic Properties

Thermodynamic properties of liquid mixtures are completely defined by the binary DCFI. However, statistical mechanics does not provide a means to evaluate these properties except for rigid body systems.[27] The experimental behavior of the like and unlike DCFI can be determined through the simultaneous knowledge of the volumetric properties and activity coefficient. From Campanella,[163]

$$1 - C_{11} = \frac{\bar{v}_1^2}{v\kappa_T RT} + x_2 \frac{d\ln\gamma_1}{dx_1}\bigg|_{T,P} \qquad (6\text{-}1)$$

$$1 - C_{12} = \frac{\bar{v}_1\bar{v}_2}{v\kappa_T RT} + x_1 \frac{d\ln\gamma_1}{dx_2}\bigg|_{T,P} \qquad (6\text{-}2a)$$

$$= \frac{\bar{v}_1\bar{v}_2}{v\kappa_T RT} + x_2 \frac{d\ln\gamma_2}{dx_1}\bigg|_{T,P} \qquad (6\text{-}2b)$$

$$1 - C_{22} = \frac{\bar{v}_2^2}{v\kappa_T RT} + x_1 \frac{d\ln\gamma_2}{dx_2}\bigg|_{T,P} \qquad (6\text{-}3)$$

where the volume variable of the DCFI is here obtained from the pressure variable. These formal relationships may cause some difficulties in the evaluation of the binary DCFI due to the lack of available good quality experimental information. The alternative is to use the Van der Waals one-fluid concept in the corresponding states approach. The mixture is considered to be a hypothetical pure liquid and the reduced DCFI for the mixture is given as

$$C_m = C_m^* f(\rho V_m^*, T_m^*/T) \qquad (6\text{-}4a)$$

where

$$V_m^* = \sum_i \sum_j x_i x_j \left(\frac{V_i^* + V_j^*}{2}\right)(1-k_{ij}) \qquad (6\text{-}4b)$$

$$C_m^* = \sum_i x_i C_i^* \qquad (6\text{-}4c)$$

$$T_m^* = \sum_i x_i T_i^* \qquad (6\text{-}4d)$$

In the case of the binary parameter $k_{ij}=0$, the volume parameter reduces to

$$V_m^* = \sum_i x_i V_i^* \tag{6-4e}$$

From Equation (6-4), the bulk modulus of liquid mixtures can be written as

$$\kappa_{Tm}^{-1} = \rho RT(1-C_m) \tag{6-5}$$

and the pressure expression for the compressed liquid mixtures is given as

$$\frac{P-P_o}{RT} = (\rho-\rho_o) - C_m^* g(\rho V_m^*, T_m^*/T; \rho_o) \tag{6-6}$$

where the function g is the integral from ρ_o to ρ of the function f in Equation (6-4a). The pressure dependence of the excess volume at constant temperature and composition is given as

$$-\frac{\partial V^E}{\partial P} = \frac{1}{\rho^2(1-C_m)RT} - \sum_i \frac{x_i}{\rho_i^2(1-C_i)RT} \tag{6-7}$$

where the subscript i denotes a pure component property. This function can reproduce the variations shown in Figure 3-8. The partial molar volume can be calculated as

$$\bar{v}_i = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

$$= -\frac{\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}}}{\left(\frac{\partial P}{\partial V}\right)_{T,\underline{N}}}$$

$$= V\kappa_{Tm}\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}} \qquad (6\text{-}8)$$

where N_i is the number of moles of component i.

For the binary liquid mixtures, the DCFI can be related to the Helmholtz free energy.

$$C_{11} = \frac{1}{x_1} - \frac{\rho V}{RT}\frac{\partial^2 A}{\partial N_1^2}\bigg|_{T,V,N_2} \qquad (6\text{-}9)$$

$$C_{22} = \frac{1}{x_2} - \frac{\rho V}{RT}\frac{\partial^2 A}{\partial N_2^2}\bigg|_{T,V,N_1} \qquad (6\text{-}10)$$

$$C_{12} = -\frac{\rho V}{RT}\frac{\partial^2 A}{\partial N_1 \partial N_2}\bigg|_{T,V}$$

$$= \frac{x_1}{x_2}\frac{\rho V}{RT}\frac{\partial^2 A}{\partial N_1^2}\bigg|_{T,V,N_2} - \frac{1}{x_2}\frac{V}{RT}\frac{\partial P}{\partial N_1}\bigg|_{T,V,N_2} \qquad (6\text{-}11a)$$

$$= \frac{x_2}{x_1}\frac{\rho V}{RT}\frac{\partial^2 A}{\partial N_2^2}\bigg|_{T,V,N_1} - \frac{1}{x_1}\frac{V}{RT}\frac{\partial P}{\partial N_2}\bigg|_{T,V,N_1} \qquad (6\text{-}11b)$$

Details of the properties from the present correlation are listed in Appendix B.

Liquid Mixture Compression Data Bank

Experimental information on the volumetric properties of compressed liquid mixtures is important in the fundamental understanding of the statistical theory, structure effects, and intermolecular interactions of solution at high pressurers.[164] However, there are considerably fewer liquid mixture compression data than there are for pure components. The present data bank contains 34 binary systems. They are arranged in the order of increasing complexity of the intermolecular interactions and listed in the first column of Table 6-1. These include simple liquid mixtures from Streett and his coworkers,[49,75,76,88,89] n-alkane mixtures from Dymond et al.,[131,133] mixtures of various C_6 compounds from Matsuo and Van Hook,[118] mixtures of benzene and its derivatives from Takagi and his coworker,[115,116] mixtures of alcohol and hydrocarbons from Ozawa et al.,[50] and acqueous solutions of alcohols from Makita and his coworkers.[91,97] The experimental accuracy of the mixture data is high except for those systems where the volumetric data are derived from ultrasonic velocity measurements.[116]

Results and Discussions

The extension of the pressure equation to mixtures by using the mixing rules in Equation (6-4) has been applied to

Table 6-1

Binary Parameters and Comparisons with Liquid Mixtures Compression Data

System	Data Range T,°K	Data Range P,bar	No. of Points	Eq(6-4e) AAE,%	Eq(6-4b) AAE,%	k_{ij}x100	ref.
Argon + Krypton	129-147	33-1506.5	86	0.9342	0.8774	0.0381	76
Methane + Krypton	129-147	25.2-1176.9	58	0.6301	0.4722	0.0895	89
Argon + Methane	110-120	10-1379	152	2.5461	0.7082	-0.6496	75
Carbon monoxide + Methane	116-125	20-1600	108	1.6202	1.7949	0.1146	49
Nitrogen + Methane	110-120	14.5-1379	64	2.6275	1.1376	-0.6000	88
n-Hexane + n-Hexadecane	298-373	1-4908	111	3.2069	2.5566	0.3740	126
n-Decane + n-Hexadecane	348-373	1-4228	16	0.9806	0.8551	-0.3317	131
n-Octane + n-Dodecane	298-373	1-4126	32	2.0602	2.3738	-0.2720	131
n-Hexane + n-Dedecane	298-348	1-4360	14	1.7381	1.1389	-0.4030	131
Isooctane + n-Dodecane	298-373	1-6053	50	2.1885	2.1243	-0.0450	133
n-Decane + n-Tetradecane	298-358	1.01-4301	104	4.7150	4.7373	0.0187	165
n-Dodecane + n-Hexadecane	298-358	1.01-3313	84	2.0050	1.9837	0.0380	165
n-Heptane + Methylcyclo-pentane	298-348	1-1962	266	1.9289	1.5927	-0.3104	50
Benzene-d_6 + Benzene	348	1-3404	7	3.8790	1.8476	-0.6100	114
	288	1-350	24	0.3085	0.1638	0.1055	118
Benzene + Cyclohexane	298-348	1-1056	144	1.6842	1.6608	-0.0670	117
	288-313	1-350	72	2.2889	0.4037	-0.5580	118

Table 6-1 (Continued)

System	Data Range T,°K	Data Range P,bar	No. of Points	Eq(6-4e) AAE,%	Eq(6-4b) AAE,%	k_{ij}x100	ref.
Cyclohexane + Benzene-d_6	288-313	1-350	72	1.1170	0.3059	-0.2580	118
Cyclohexane + n-Hexane	298-348	1-5000	60	2.2815	1.8112	-0.5630	120
3,3-Diethylpentane + 4,4-Dipropylheptane	303-423	0-8000	81	1.0991	0.5226	0.2427	43
Carbon tetrachloride + Octamethylcyclo-tetrasiloxane	313-373	1.01-2344.5	108	0.9579	0.9095	0.1000	81
Toluene + Benzene	293-313	1-2000	122	2.6616	1.6817	-0.5960	116
o-Xylene + Benzene	293-313	1-2000	76	2.2319	1.0071	-0.6070	116
Hexafluorobenzene + Benzene	298-373	1-3036	109	2.8151	2.8376	-0.5200	114
Chlorobenzene + Benzene	303	1-2000	82	3.7074	1.6405	0.9910	115
Bromobenzene + Benzene	303	1-2000	83	5.7698	2.6665	1.5170	115
Nitrobenzene + Benzene	293-313	1-2000	142	6.3348	2.5576	1.8600	115
Aniline + Nitrobenzene	298-358	0-1000	144	1.1480	0.2866	-0.3466	166
Ethanol + n-Hexane	298-348	1-1962	131	3.6231	3.7142	-0.2150	50
Methylcyclopentane + Ethanol	298-348	1-1962	265	3.1555	2.7995	-0.8200	50

Table 6-1 (Continued)

System	Data Range T,°K	Data Range P,bar	No. of Points	Eq(6-4e) AAE,%	Eq(6-4b) AAE,%	k_{ij}x100	ref.
Methanol + Water	283-348	1-2076	128	7.1397	4.0353	2.1660	91
	278-323	1-2750	210	5.4796	3.5892	1.7750	92
Ethanol + Water	298-323	1-3486	206	6.2708	3.7903	1.9056	97
Methyl ethyl ketone + Water	303-343	0-1720	106	9.8476	6.3322	-7.7880	105

all of the compressed liquid mixtures in the present data bank. Table 6-1 summarizes the results with and without a binary parameter k_{ij}. The predicted results from the simple mixing rules are listed in the fifth column of the table. The results are quite good. There is a definite relationship of the prediction and the accuracy of correlating the pure component compressions. The average absolute percent deviation (AAE%) increases with increasing complexity of the binary system.

For simple liquid mixtures, the agreement between the experiment and calculated pressures is as good as the individual pure component. The Argon-Methane system is the only exception. The relatively large deviation is probably due to experimental uncertainty which is not cited in the original papers.[75] There is a striking feature in the pressure dependence of excess volume in these binary systems. The excess volume is negative at low pressures and rises rapidly with increasing pressure. At pressures above a certain value, there is very little variation of the excess volume on temperature or pressure. The present correlation does reproduce the behavior described above though the decreasing value of $\partial V^E/\partial P \mid T,\underline{x}$ can be faster or slower than the data show.

For n-alkane mixtures, the deviations tend to increase with increasing difference in the chain length. Use of the volume fraction instead of mole fraction average in the temperature parameter improves the predicted results for all

of n-alkane mixtures tested. This is associated with the Van der Waals forces between the segments instead of the molecules.[167] The reduced temperature of a binary mixture is given as

$$\tilde{T} = \sum_i \varphi_i \tilde{T}_i \qquad (6\text{-}12)$$

where

$$\varphi_i = \frac{x_i V_i^*}{\sum_{i=1}^{2} x_i V_i^*} \qquad (6\text{-}13)$$

From Equations (6-12) and (6-13), the characteristic temperature of the binary mixture then can be written as

$$T_m^* = \frac{T_1^* T_2^* (x_1 V_1^* + x_2 V_2^*)}{x_1 V_2^* T_1^* + x_2 V_1^* T_2^*} \qquad (6\text{-}14)$$

The Principle of Congruence[164] works out very well only for this type of mixture.

For mixtures of C_6 compounds, the present correlation can indicate the presence of order arising from the nature of the packing volume at compressed states. Physically, order corresponds to a cohesion which decreases the volume of a liquid.[168] Evaluation of the deviation pattern

reveals the fact that the calculated pressure is systematically lower than the experimental pressure up to highest pressures measured. This is because the experimental volume is consistently lower than the calculated volume at a given pressure, temperature, and composition since the simple mixing rules do not include the order that appears. However, adjustment of mixture volume by taking into account a binary parameter in the quadratic mole fraction average of the volume parameter improves the overall deviations. The results are as good as the pure component correlation.

For nonpolar mixtures of globular species, the predicted results are comparable to those of the pure component and are independent of the size difference of the molecules. This is the case of carbon tetrachloride-octamethylcyclotetrasiloxane[81] in which the latter has a characteristic volume more than three times of the former. For mixtures of benzene and its derivatives, the deviations increase with increasing polarity of the substituents. The large deviation is due probably to the experimental imprecision, which is associated with an anomaly observed in the ultrasonic velocity measurements.[116] For alkane-alkanol mixtures, the predicted results are acceptable if the nonideality and experimental inaccuracies are allowed for. The experimental excess volume varies with composition in a complicated manner and nonideality is significant only at pressures below 1 kbar.

The deviation is proportional to the absolute value of the ambient excess volume at the given composition. For mixtures of aniline-nitrobenzene, the pure T* and C* values are very similar to each other; the only difference is in V*. Though the predicted results have only about 1% error, it is not as good as the accuracy of the experiental data. Use of one binary parameter in the composition dependence of volume parameter does improve the result to as good as the pure component. For aqueous systems, the state dependence of the volumetric properties is even more complicated though predictions within 10% error are always obtained.

The results with a fitted binary parameter in the composition dependence of the volume parameter are listed in the sixth column of Table 6-1. For most of the systems, the correlated results are much improved in comparison with the predicted results and one binary parameter is enough. For those systems with complicated state dependence, more than one binary parameter would be required for agreement within experimental uncertainty. Though use of three binary parameters in the composition dependence of the three characteristic parameters would completely recover the same accuracy as the pure component correlation for each composition, predictive capability is missing completely.

CHAPTER 7
CONCLUSIONS AND RECOMMENDATIONS

This work has focused on the development of a general and accurate liquid phase equation of state which is based on an unique approach of the statistical mechanical direct correlation function integrals. Two treatments have been adopted to model the liquid DCFI: the corresponding states principle and the group contribution method. The major engineering contribution of the present work is the construction of a three-parameter corresponding states correlation which is based on the detailed analysis of the experimental DCFI in the compressed liquid phase. The molecular corresponding states correlation either in compressibility form (Chapter 4) or in pressure form (Chapter 5) has been shown to be the most accurate in representing the volumetric properties of compressed liquids and liquid mixtures.

In the absence of a rigorous site-site interaction model for the direct correlation function, this work developed an empirical parameter-additive group contribution corresponding states correlation arising from the appearance of the group-additive crossover parameters. The group contribution corresponding states correlation

has been shown to be successful in the prediction of the volumetric properties of compressed liquid n-alkanes in which the molecular characteristic temperature can be estimated. However, application to the other substances is still hampered by a lack of knowledge about the characteristic temperature. In practical use, the alternative is to make one compression measurement to determine the characteristic temperature while characteristic volume and DCFI can be estimated from the group parameters listed in Table 5-5.

An important by-product in the process of the group contribution formulation is the establishment of an extensive data bank for the volumetric properties of compressed liquids and liquid mixtures. The experimental PVT data, either from direct or indirect measurements, have been carefully evaluated and converted to common units, bar-cm^3/mol-°k.

The most important scientific contribution of this work is the finding of the crossover behavior of the compressed liquid isotherms. For every liquid, there exists a unique density where the reduced bulk modulus is independent of temperature. Thus the compressional properties of a real liquid do not behave like those of a rigid body fluid. Furthermore, the assumption of linear density behavior of dense liquid[169,170] is not fully correct. In fact, while there exists a transition region of density in which the volumetric behavior of compressed

liquid may be linear in density, below or above this region the corrections for the nonlinear density behavior have to be introduced.

Thermodynamic properties of major interest have been derived from the present correlation. For pure liquids, the compressional thermodynamic properties can be predicted from the data along the orthobaric curve. For liquid mixtures, the excess thermodynamic properties can be calculated along with specific mixing rules for the known pure component properties. The correlation method also provides a way to estimate the binary DCFI which can be related to the thermodynamic derivative properties in the fluctuation solution theory.

The above conclusions indicate our present concept of compressed liquid properties. There are some suggestions for future work.

1. To rework the form of the polynomial to have all isotherms pass through the crossover point. Currently, extrapolation of the present correlation to the temperature below the freezing point of methane does vary away from this point. The revised formula will be given as

$$\frac{C^*-C}{1-C^*} = \sum_{i=1}^{m} \sum_{j=1}^{n} a_{ij} \tilde{\tau}^{j-1} (\tilde{\rho}-1)^i \qquad (7\text{-}1)$$

This ensures that all isotherms will pass through the crossover point. Application to low temperatures ($\tilde{T}<0.5$) would be more reliable with the modified correlation.

2. To investigate thoroughly the pressure dependence of excess volume for compressed liquid mixtures. An empirical correction which could be used to estimate the excess volume of compressed liquid mixtures from that of atmospheric measurement would improve the accuracy of the present correlation, especially for those mixtures with complicated variations of the excess volume.

3. To apply the present correlation to the calculation of partial molar volume and chemical potential and compare with experimental data for compressed liquid mixtures. This would be a strong test of the model's reliability.

4. To optimize the present group parameters and determine the molecular characteristic temperature for the rest of substances. While the relative insensitivity of dense liquid results to the characteristic temperature means the present group contribution corresponding states method may find useful application in predictive work, refinement of the group method would ensure its value.

APPENDIX A
PERCUS-YEVICK HARD SPHERE DIRECT CORRELATION FUNCTION INTEGRAL FROM VERLET-WEIS ALGORITHM

Verlet and Weis[2] have presented a simple algorithm to calculate the effective hard sphere diameter $d(\rho,T)$ from Weeks-Chandler-Andersen (WCA) perturbation theory. Define a temperature dependent hard sphere diameter as

$$d_R(T) = \int_0^\infty [1 - \rho^{-\frac{u_o(x)}{kT}}]dx \qquad (A\text{-}1)$$

where $x=r/\sigma$, r is the separation distance, σ is the collision diameter, and $u_o(x)$ is the WCA reference potential. Verlet and Weis show that this can be simulated by the empirical expression.

$$d_R = \frac{0.3837+1.0680}{0.4293+\theta} \qquad (A\text{-}2)$$

where

$$\theta = \varepsilon/kT$$

The density dependence of the WCA values of hard sphere diameter to first order is given by

$$d = d_R(1+Y\delta) \tag{A-3}$$

where

$$\delta = \frac{1}{210.21+404.60} \tag{A-4}$$

$$Y = \frac{1-4.25\eta_\omega+1.362\eta_\omega^2 -0.8751\eta_\omega^3}{(1-\eta_\omega)^2} \tag{A-5}$$

$$\eta_\omega = \eta - \frac{1}{16}\eta^2 \tag{A-6}$$

$$\eta = \frac{\pi}{6}\rho d^3 \tag{A-7}$$

where η is the packing fraction. A few iterations are sufficient to find d. Then the Percus-Yevick hard sphere DCFI can be calculated as

$$C_{hs}^{PYC} = -\frac{\eta(2+\eta^2)(4-\eta)}{(1-\eta)^4} \tag{A-8}$$

where the superscript PYC is the Percus-Yevick compressibility equation and the subscript hs is hard sphere.

APPENDIX B
THERMODYNAMIC PROPERTIES OF COMPRESSED LIQUID MIXTURES FROM DCFI MODEL

From Equation (6-4), the DCFI model can be written as

$$\tilde{C} = a_0 + a_1\tilde{\rho} + a_2\tilde{\rho} + a_3\tilde{\rho}^3 \qquad \text{(B-1)}$$

where the reduced density coefficient a_i are

$$a_0 = 9.8642 - 10.191\tau - 1.5356\tau^2$$

$$a_1 = -28.465 + 30.864\tau + 6.0294\tau^2$$

$$a_2 = 27.542 - 32.898\tau - 8.7130\tau^2$$

$$a_3 = -8.2606 + 12.737\tau + 4.0170\tau^3$$

and

$$\tau = \frac{T^*}{T}$$

The pressure equation is given as

$$P = P_o + \rho^*RT\{(\tilde{\rho} - \tilde{\rho}_o) - C^*[a_o(\tilde{\rho} - \tilde{\rho}_o) + \frac{a_1}{2}(\tilde{\rho}^2 - \tilde{\rho}_o^2)$$

$$+ \frac{a_2}{3}(\tilde{\rho}^3 - \tilde{\rho}_o^3) + \frac{a_3}{4}(\tilde{\rho}^4 - \tilde{\rho}_o^4)]\} \qquad (B\text{-}2)$$

The change of Hemholtz free energy is given as

$$\frac{A-A_o}{RT} = (\frac{\tilde{\rho}_o}{\tilde{\rho}} - 1) - \ln\frac{\tilde{\rho}_o}{\tilde{\rho}} - \frac{P_o}{\rho^*RT}(\frac{1}{\tilde{\rho}} - \frac{1}{\tilde{\rho}_o}) - C^*[a_o \ln\frac{\tilde{\rho}_o}{\tilde{\rho}}$$

$$-(a_o + \frac{a_1}{2}\tilde{\rho}_o + \frac{a_2}{3}\tilde{\rho}_o^2 + \frac{a_3}{4}\tilde{\rho}_o^3)(\frac{\tilde{\rho}_o}{\tilde{\rho}} - 1) + \frac{a_1}{2}(\tilde{\rho} - \tilde{\rho}_o)$$

$$+ \frac{a_2}{6}(\tilde{\rho}^2 - \tilde{\rho}_o^2) + \frac{a_3}{12}(\tilde{\rho}^3 - \tilde{\rho}_o^3)] \qquad (B\text{-}3)$$

For binary mixtures, the simple mixing rules are given as

$$V^* = x_1 V_1^* + x_2 V_2^* \qquad (B\text{-}4)$$

$$C^* = x_1 C_1^* + x_2 C_2^* \qquad (B\text{-}5)$$

$$T^* = x_1 T_1^* + x_2 T_2^* \qquad (B\text{-}6)$$

Thermodynamic properties of mixtures then can be obtained through the following relationships.

$$\left.\frac{\partial^2 A}{\partial V^2}\right|_{T,\underline{N}} = -\left.\frac{\partial P}{\partial V}\right|_{T,\underline{N}} = \frac{\rho}{N\varkappa_T}$$

$$= \frac{\rho RT}{V}[1-C^*(a_o+a_1\tilde{\rho}+a_2\tilde{\rho}^2+a_3\tilde{\rho}^3)] \qquad \text{(B-7)}$$

$$\frac{\partial A}{\partial V}\left(\left.\frac{\partial A}{\partial N_1}\right|_{T,V,N_2}\right)_{T,\underline{N}} = -\left.\frac{\partial P}{\partial N_1}\right|_{T,V,\underline{N}_2} = -\frac{\rho\bar{v}_1}{N\varkappa_T}$$

$$= -\frac{RT}{V}\left[1-(C_1^*a_o+C^*a_o')-\frac{1}{2}(C_1^*a_o\tilde{\rho}+C^*a_1\tilde{\rho}_1+C^*a_1'\tilde{\rho})\right.$$

$$(1+\frac{\tilde{\rho}_o}{\tilde{\rho}})-\frac{1}{3}(C_1^*a_2\tilde{\rho}^2+2C^*a_2\tilde{\rho}\tilde{\rho}_1+C^*a_2'\tilde{\rho}^2)(1+\frac{\tilde{\rho}_o}{\tilde{\rho}}+\frac{\tilde{\rho}_o^2}{\tilde{\rho}^2}) -$$

$$\left.\frac{1}{4}(C_1^*a_3\tilde{\rho}^3+3C^*a_3\tilde{\rho}^2\tilde{\rho}_1+C^*a_3'\tilde{\rho}^3)(1+\frac{\tilde{\rho}_o}{\tilde{\rho}}+\frac{\tilde{\rho}_o^2}{\tilde{\rho}^2}+\frac{\tilde{\rho}_o^3}{\tilde{\rho}^3})\right](1-\frac{\tilde{\rho}_o}{\tilde{\rho}}) \qquad \text{(B-8)}$$

where

$$a_o' = 9.8642 - 10.191\tau_1 - 3.0712\tau\tau_1$$

$$a_1' = -28.465 + 30.864\tau_1 + 12.0588\tau\tau_1$$

$$a_2' = 27.542 - 32.898\tau_1 - 17.426\tau\tau_1$$

$$a_3 = -8.2606 + 12.737\tau_1 + 8.0340\tau\tau_1$$

and

$$\tilde{\rho}_1 = \frac{V_1^*}{V}$$

$$\tau_1 = \frac{T_1^*}{T}$$

From Equations (B-5) and (B-6), the partial molar volume can be calculated as

$$\bar{v}_1 = \left(\frac{\partial V}{\partial N_1}\right)_{T,P,N_2}$$

$$= -\frac{\left(\frac{\partial P}{\partial N_1}\right)_{T,V,N_2}}{\left(\frac{\partial P}{\partial V}\right)_{T,\underline{N}}}$$

$$= \frac{\left(1-\frac{\tilde{\rho}_o}{\tilde{\rho}}\right)}{\rho[1-C^*(a_o+a_1\tilde{\rho}+a_2\tilde{\rho}^2+a_3\tilde{\rho}^3)]}\,[1-(C_1^*a_o+C^*a_o')-$$

$$\tfrac{1}{2}(C_1^*a_1\tilde{\rho}+C^*a_1\tilde{\rho}_1+C^*a_1'\tilde{\rho})\left(1+\frac{\tilde{\rho}_o}{\tilde{\rho}}\right)-$$

$$\tfrac{1}{3}(C_1^*a_2\tilde{\rho}^2+2C^*a_2\tilde{\rho}\tilde{\rho}_1+C^*a_2'\tilde{\rho}^2)\left(1+\frac{\tilde{\rho}_o}{\tilde{\rho}}+\frac{\tilde{\rho}_o^2}{\tilde{\rho}^2}\right)-$$

$$\tfrac{1}{4}(C_1^*a_3\tilde{\rho}^3+3C^*a_3\tilde{\rho}^2\tilde{\rho}_1+C^*a_3'\tilde{\rho}^3)\left(1+\frac{\tilde{\rho}_o}{\tilde{\rho}}+\frac{\tilde{\rho}_o}{\tilde{\rho}^2}+\frac{\tilde{\rho}_o^3}{\tilde{\rho}^3}\right)] \qquad \text{(B-9)}$$

$$\frac{\mu_1}{RT} = \frac{1}{RT}\left.\frac{\partial A}{\partial N_1}\right|_{T,V,N_2}$$

$$= [1-(C_1^* a_0 + C^* a_0')]\ln\frac{\tilde{\rho}}{\tilde{\rho}_0} - [1-(C_1^* a_0 + C^* a_0') -$$

$$\frac{1}{2}(C_1^* a_1 \tilde{\rho}_0 + C^* a_1 \tilde{\rho}_0' + C^* a_1' \tilde{\rho}_0)$$

$$-\frac{1}{3}(C_1^* a_2 \tilde{\rho}_0^2 + 2C^* a_2 \tilde{\rho}_0 \tilde{\rho}_0' + C^* a_2' \tilde{\rho}_0^2) -$$

$$\frac{1}{4}(C_1^* a_3 \tilde{\rho}_0^3 + 3C^* a_3 \tilde{\rho}_0^2 \tilde{\rho}_0' + C^* a_3' \tilde{\rho}_0^3)](1-\frac{\tilde{\rho}_0}{\tilde{\rho}}) -$$

$$\frac{1}{2}(C_1^* a_1 \tilde{\rho} + C^* a_1 \tilde{\rho}' + C^* a_1' \tilde{\rho})(1-\frac{\tilde{\rho}_0}{\tilde{\rho}}) -$$

$$\frac{1}{6}(C_1^* a_2 \tilde{\rho}^2 + 2C^* a_2 \tilde{\rho}\tilde{\rho}_1 + C^* a_2' \tilde{\rho}^2)(1-\frac{\tilde{\rho}_0^2}{\tilde{\rho}^2}) -$$

$$\frac{1}{12}(C_1^* a_1 \tilde{\rho}^3 + 3C^* a_3 \tilde{\rho}^2 \tilde{\rho}_1 + C^* a_3' \tilde{\rho}^3)(1-\frac{\tilde{\rho}_0^3}{\tilde{\rho}^3}) \qquad \text{(B-10)}$$

where

$$\tilde{\rho}_0' = \frac{V_1^*}{V_0}$$

$$\left.\frac{\partial^2 A}{\partial N_1^2}\right|_{T,V,N_2} = \left.\frac{\partial \mu_1}{\partial N_1}\right|_{T,V,N_2}$$

$$= \frac{RT}{\rho V}\{(2C_1^* a_o' + C^* a_o'')\ln\frac{\tilde{\rho}_o}{\tilde{\rho}} + [(2C_1^* a_o' + C^* a_o'') + \tfrac{1}{2}(2C_1^* a_1\tilde{\rho}_o' + 2C_1^* a_1'\tilde{\rho}_o$$

$$+ 2C_1^* a_1'\tilde{\rho}_o' + C^* a_1''\tilde{\rho}_o) + \tfrac{1}{3}(4C_1^* a_2\tilde{\rho}_o\tilde{\rho}_o' + 2C_1^* a_2'\tilde{\rho}_o^2 + 2C^* a_2\tilde{\rho}_o'^2 +$$

$$4C^* a_2'\tilde{\rho}_o\tilde{\rho}_o' + C^* a_2''\tilde{\rho}_o^2) + \tfrac{1}{4}(6C_1^* a_3\tilde{\rho}_o^2\tilde{\rho}_o' + 2C_1^* a_3'\tilde{\rho}_o^3 + 6C^* a_3\tilde{\rho}_o\tilde{\rho}_o'^2 +$$

$$6C_1^* a_3'\tilde{\rho}_o^2\tilde{\rho}_o' + C^* a_3''\tilde{\rho}_o^3)](1-\frac{\tilde{\rho}_o}{\tilde{\rho}}) - \tfrac{1}{2}(2C_1^* a_1\tilde{\rho}_1 + 2C_1^* a_1'\tilde{\rho} + C^* a_1''\tilde{\rho}) -$$

$$(1-\frac{\tilde{\rho}_o}{\tilde{\rho}}) - \tfrac{1}{6}(4C_1^* a_2\tilde{\rho}\tilde{\rho}_1 + 2C_1^* a_2'\tilde{\rho}^2 + 2C^* a_2\tilde{\rho}_1^2 + 4C^* a_2'\tilde{\rho}\tilde{\rho}_1 + C^* a_2''\tilde{\rho}^2)$$

$$(1-\frac{\tilde{\rho}_o^2}{\tilde{\rho}^2}) - \frac{1}{12}(6C_1^* a_3\tilde{\rho}^2\tilde{\rho}_1 + 2C_1^* a_3'\tilde{\rho}^3 + 6C^* a_3\tilde{\rho}\tilde{\rho}_1^2 + 6C^* a_3'\tilde{\rho}^2\tilde{\rho}_1 + C^* a_3''\tilde{\rho}^3)$$

$$(1-\frac{\tilde{\rho}_o^3}{\tilde{\rho}^3}) \qquad \text{(B-11)}$$

where

$$a''_0 = 9.8642 - 10.191\tau_1 - 3.0712\tau_1^2$$

$$a''_1 = -28.465 + 30.864\tau_1 + 12.0588\tau_1^2$$

$$a''_2 = 27.542 - 32.898\tau_1 - 17.426\tau_1^2$$

$$a''_3 = -8.2606 + 12.737\tau_1 + 8.0340\tau_1^2$$

Comparison of Equations (B-7), (B-8), and (B-11) with the following equations,

$$\left.\frac{\partial^2 A}{\partial V^2}\right|_{T,\underline{N}} = -\left.\frac{\partial P}{\partial V}\right|_{T,\underline{N}}$$

$$= \frac{\rho RT}{V}(1-x_1^2 C_{11}-2x_1 x_2 C_{12}-x_2^2 C_{22}) \qquad \text{(B-12)}$$

$$\left.\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial N_1}\right|_{T,V,N_2}\right)\Bigg|_{T,\underline{N}} = -\left.\frac{\partial P}{\partial N_1}\right|_{T,V,N_2}$$

$$= -\frac{RT}{V}(1-x_1 C_{11}-x_2 C_{12}) \qquad \text{(B-13)}$$

$$\left.\frac{\partial^2 A}{\partial N_1^2}\right|_{T,V,N_2} = \left.\frac{\partial \mu_1}{\partial N_1}\right|_{T,V,N_2}$$

$$= \frac{RT}{\rho V}\left(\frac{1}{x_1} - C_{11}\right) \qquad \text{(B-14)}$$

The binary DCFI then can be calculated.

Appendix C

Computer Programs

```
C     VOLUMETRIC PROPERTIES OF ARGON USING THE STROBRIGE EQUATION
C     REF: TWU ET. AL. FLUID PHASE EQUILIBRIA, 4(1980)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(16)
      DATA A/1.31024,-3.80636,-2.37238,-0.798872,0.198761,
     1  1.47014,-0.786367,2.19465,5.75429,6.78220,-9.94904,
     1  -15.6162,86.6430,18.5270,9.04755,8.68282/
      DO 2 I=1,8
      READ(5,*) T
      PM=0.6890606D0*2078.76667D0*((T/83.80D0)**1.59817868D0
     1-1.0D0)
      TR=T/150.86D0
      TS=1.2593D0*TR
      WRITE(6,101) T,PM
  101 FORMAT(2X,2F13.4/)
      TI=1.0D0/TS
      F1=A(1)+TI*(A(2)+TI*(A(3)+TI*(A(4)+A(5)*TI*TI)))
      F2=A(6)+A(7)*TI
      F3=A(8)
      F4=TI*TI*TI*(A(9)+TI*(A(10)+A(11)*TI))
      F5=TI*TI*TI*(A(12)+TI*(A(13)+A(14)*TI))
      F6=A(15)*TI
      DO 1 N=1,40
      READ(5,*) V
      RR=1.0D0/(0.01341D0*V)
      RS=0.3189D0*RR
      R2=RS*RS
      R3=RS*R2
      R4=RS*R3
      R5=RS*R4
      D1=-A(16)*R2
      E1=DEXP(D1)
      F=1.0D0+F1*RS+F2*R2+F3*R3+F4*R2*E1+F5*R4*E1+F6*R5
      DF=F1+2.0D0*F2*RS+3.0D0*F3*R2+F4*E1*(2.0D0*RS-2.0D0
     1*A(16)*R3)+F5*E1*(4.0D0*R3-2.0D0*A(16)*R5)+5.0D0*F6*R4
      OMC=RS*DF+F
      P=F*RR*13.41D0*0.0831434D0*T
      IF(P.GT.PM) GO TO 1
      C=1.0D0-OMC
      WRITE(6,5) V,P,C
    5 FORMAT(3F13.4)
    1 CONTINUE
    2 CONTINUE
      STOP
      END
```

```
C      MOLLERUP'S PROGRAM TO GENERATE THE DCFI DATA OF METHANE
C      PROGRAM METHERM
C      PRINTOUT ISOTHERMS.
       IMPLICIT REAL*8 (A-H,O-Z)
       COMMON/ONE/AG,AL,BB,BE,DE,GK,  TTRP,PTRP,DTRP,  TCRT,PCRT,DCRT
       COMMON/THRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPSIDR,  XB1,XB2,XD1,XD2
       COMMON/SIX/GP,G,GY,GX,GXX
     9 FORMAT(1X,3F13.4)
       CALL METHAN
       DO 130 I=1,3
       READ (5,*) TT
       PM=0.117435675+1909.40*((TT/90.68)**1.85-1.0)
       IF(TT-TCRT) 103,103,104
   103 DG=DENGAS(TT)
       DL=DENLIQ(TT)
   104 DO 120 N=1,34
       READ(5,*) VV
       DN=1000.0D0/VV
       IF(TT-TCRT) 114,115,115
   114 IF(DN.GT.DG.AND.DN.LT.DL) GO TO 120
   115 PP = DPDRF(TT,DN)
       IF(PP.GT.PM) GO TO 130
       WRITE(6,9) VV,PP,GY
   120 CONTINUE
   130 CONTINUE
       STOP
       END
       SUBROUTINE METHAN
C     NOTE THAT PRESSURES ARE IN BARS, 1 ATM = 1.01325 BAR.
C     ONE BAR-LITER = 100 JOULES.
       IMPLICIT REAL*8 (A-H,O-Z)
       COMMON A1,A2,A3,A4,B1,B2,B3,B4,C1,C2,C3,C4,C5,C6,D1,D2,D3,D4,D5
       COMMON/ONE/AG,AL,BB,BE,DE,GK,  TTRP,PTRP,DTRP,  TCRT,PCRT,DCRT
       COMMON/THRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPSIDR,  XB1,XB2,XD1,XD2
       COMMON/FIVE/ P,T,DEN,DPDD,  E,H,S,  CV,CP,W,  WK
       COMMON/EIGHT/ DDLDT
C     CONSTANTS FROM MARSHGAS 9/3/71.
       WRITE(6,99)
    99 FORMAT(31H  *** CH4 ***  FEBRUARY 22 1983                  )
       TTRP=90.68
       PTRP=0.117435675
       DTRP=28.1472
C     PCRT = 45.956467   BAR
       TCRT=190.53
       PCRT=PSATF(TCRT)
       DCRT=10.15
       AG=.5
       AL=.5
       BB=0.8
       BE=4.0
       DE=1.2
        GK = 0.0831434
        CJ = 100
        WK = 101325/16.043
       A1=-4.15452847
       A2=-4.77390186
       A3=3.51999044
       A4=4.25737412
       B1=1.74744656
       B2=2.57679569
```

```
      B3=0.46538980
      C1=5.10335931
      C2=-12.4202274
      C3=6.36124273
      D1=1.88383919
      D2=-3.54713477
      D3=1.07408815
      RETURN
      END
      FUNCTION PSATF(T)
C     METHANE VAPOR PRESSURE VIA PRYDZ/GOODWIN DATA, NOV., 1970.
C     NOTE,   PRESSURE IN BARS,    1.01325 BAR/ATM.
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/THRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPSIDR, XB1,XB2,XD1,XD2
      DATA  PTRP / 0.117435675/, TTRP/90.68/, TCRT/190.53/, E/1.5/
      DATA  A/4.77325537, B/1.7665879/, C/-0.5702812/, D/1.3311873/
    1 XK=1-TTRP/TCRT
      X=(1-TTRP/T)/XK
      G=1-X
      IF(G) 2,3,4
    2 PSATF = 0
      DPDT = 0
        RETURN
    3 W=0
      W1=0
      GO TO 5
    4 W = G**E
        W1 = -E*W/G
    5 DXDT=TTRP/XK/T**2
       Z=X*W
       Z1 = W + X*W1
    6 FZ = A*X + B*X**2 + C*X**3 + D*Z
    7 F1 = A + 2*B*X + 3*C*X**2 + D*Z1
    8 PSATF=PTRP*DEXP(FZ)
      DPDT=PSATF*F1*DXDT
        RETURN
       END
      FUNCTION DENLIQ(T)
C     METHANE SATD. LIQUID DENSITIES VIA GOODWIN.
C     THIS FUNCTION REFITTED VIA   ,DENSATLQ,   4/29/71.
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/EIGHT/ DDLDT
      DATA TCRT/190.53/,DCRT/10.15/
      DATA  A/0.539403/, B/1.896635/, C/-0.018387/, E/0.88/
    1 X = T/TCRT
        Z = 1 - X
      IF(Z.LT..01) GO TO 7
    2 F = -B*X**2/Z
        XP = DEXP(F)
    3 DFDX = -E*(2 + X/Z)*X/Z
        Q = Z**0.36
    4 G = A*Z + B*Q + C*XP
      DENLIQ = DCRT*(1+G)
    5 G1 = C*XP*DFDX - A - 0.36*B*Q/Z
    6 DDLDT = DCRT*G1/TCRT
          RETURN
    7 IF(Z.LT.1.D-09) Z=1.D-09
      Q=Z**.36
      G=A*Z + B*Q
      DENLIQ = DCRT*(1.+G)
```

```
      G1 = -A - .36*B*Q/Z
      DDLDT = DCRT*G1/TCRT
      RETURN
        END
      FUNCTION TSATF(DEN)
C     TSAT(DEN) FORMULA,  METHANE, CONSTRAINED TO TRIPLE POINT, IPTS-68.
C     YIELDS ALSO THE FIRST DERIVATIVE RSP. TO RHO>DEN/DTRP.
C     EQN., (TCRT/T-1)/AZ = F(R) = U(S)*(1 + A1*LOG(R) + (R-1)*W(R)),
C     WHERE,  U(S) = ((S-1)/(ST-1))**(8/3),  AZ = (TCRT/TTRP-1),  AND -
C     W(R) = A2 + A3*R + ... + A8*R6.
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/ONE/AG,AL,BB,BE,DE,GK,  TTRP,PTRP,DTRP,  TCRT,PCRT,DCRT
      COMMON/THRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPSIDR,  XB1,XB2,XD1,XD2
      DIMENSION A(8)
      DATA A / -0.8142449,  2.4794529,  -6.7598384,  41.05600105,
     1 -133.4449230,  223.4955973,  -181.8267154,  58.8359684/
     1 AZ = TCRT/TTRP - 1
        DSDR = DTRP/DCRT
        SK = DSDR - 1
     2 R=DEN/DTRP
       S=DEN/DCRT
       IF((S-1)/SK.LT.0.) G=-DABS((S-1)/SK)**.333333
       IF((S-1)/SK.GE.0.) G=((S-1)/SK)**.333333
        IF(Q) 3,9,3
     3 U = G**8
        U1 = 8*DSDR*G**5/SK/3
     4 V = R-1
       W=0
       W1=0
         DO 5 K=2,8
     5 W = W + A(K)*R**(K-2)
         W1 = W1 + (K-2)*A(K)*R**(K-3)
     6 CONTINUE
       G=DLOG(R)
        F = U*(1 + A(1)*G + V*W)
     7 F1 = U1 + A(1)*(U/R + U1*G) + U*V*W1 + U*W + U1*V*W
     8 TSATF=TCRT/(1+AZ*F)
        DTSDR=-(AZ/TCRT)*F1*TSATF**2
        RETURN
     9 TSATF = TCRT
        DTSDR = 0
          RETURN
        END
       FUNCTION THETAF(DEN)
C     IF S   1, U = AG*(S-1)**3.    IF S ^ 1, U = -AL*(S-1)**3.
C     YIELDS ALSO THE FIRST DERIVATIVE RSP. TO RHO>DEN/DTRP.
       IMPLICIT REAL*8 (A-H,O-Z)
       COMMON/ONE/AG,AL,BB,BE,DE,GK,  TTRP,PTRP,DTRP,  TCRT,PCRT,DCRT
       COMMON/THRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPSIDR,  XB1,XB2,XD1,XD2
     1 S=DEN/DCRT
        DSDR = DTRP/DCRT
        IF(S) 9,9,2
     2 G=S-1
       G2=G**2
       G3=G**3
        IF(G) 3,8,4
     3 U = AG*G3
        U1 = 3*AG*G2*DSDR
          GO TO 5
     4 U = -AL*G3
```

```
      U1 = -3*AL*G2*DSDR
    5 IF(U.LT.-50.) U=-50.
      XP = DEXP(U)
       TS = TSATF(DEN)
       THETAF = TS*XP
    7 DTHDR = TS*U1*XP + DTSDR*XP
        RETURN
    8 THETAF = TCRT
       DTHDR = 0
        RETURN
    9 THETAF = 0
      DTHDR=1.E 05
       RETURN
       END
      FUNCTION PHIF(T)
C     XB = PHI  =  X*(1-EXP(-U)),  U = BB + BE/X,
C     YIELDS ALSO  DPHI/DR, DPHI/DX, AND D2PHI/DX2.
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/ONE/AG,AL,BB,BE,DE,GK, TTRP,PTRP,DTRP, TCRT,PCRT,DCRT
      COMMON/THRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPSIDR, XB1,XB2,XD1,XD2
    1 X=T/TCRT
      U=BB+BE/X
      U1=-BE/X**2
      U2=-2*U1/X
    2 XP=DEXP(-U)
       Z=1-XP
       Z1=U1*XP
       Z2=(U2-U1**2)*XP
    3 PHIF = X*Z
       XB1 = X*Z1 + Z
       XB2 = X*Z2 + 2*Z1
    9 RETURN
        END
      FUNCTION PSIF(T,DEN)
C     XD = PSI  =  (1-W*LOG(1+1/W))/X,    W = (T-TH)/(DE*TCRT).
C     YIELDS ALSO XD1 > DPSI/DX, XD2 > D2PSI/DX2, AND DPSI/DR.
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/ONE/AG,AL,BB,BE,DE,GK, TTRP,PTRP,DTRP, TCRT,PCRT,DCRT
      COMMON/THRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPSIDR, XB1,XB2,XD1,XD2
    1 TH = THETAF(DEN)
       W = (T-TH)/DE/TCRT
        IF(W) 2,2,3
    2 PSIF=1
      XD1=0
      XD2=0
      DPSIDR=0
       RETURN
    3 X=T/TCRT
      DWDR=-DTHDR/DE/TCRT
      DWDX=1/DE
    4 U=1/X
      DUDX=-U/X
      D2UDX2=-2*DUDX/X
    5 G=DLOG(1.0D0+1.0D0/W)
       WS = 1+W
       V = 1-W*G
    6 DVDW = 1/WS-G
       D2VDW2 = 1/W/WS**2
       PSIF = U*V
    7 DPSIDR = U*DVDW*DWDR
```

```
      XD1 = U*DVDW*DWDX + V*DUDX
    8 XD2 = U*D2VDW2*DWDX**2 + 2*DUDX*DVDW*DWDX + V*D2UDX2
    9 RETURN
        END
      FUNCTION DPDRF(T,DEN)
C     NOTE,  DPDRF = PRESSURE, BAR.
C     REDUCED DERIVATIVE,  DLPDLR > R*(DP/DR)/P  IS IN COMMON.
C     (Z-1)*X/R = F(T,R) YIELDS (DP/DR)/DTRP/GK/T = 1+(R2*F1+2*R*F)/X.
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON A1,A2,A3,A4,B1,B2,B3,B4,C1,C2,C3,C4,C5,C6,D1,D2,D3,D4,D5
      COMMON/ONE/AG,AL,BB,BE,DE,GK,  TTRP,PTRP,DTRP,  TCRT,PCRT,DCRT
      COMMON/THRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPSIDR,  XB1,XB2,XD1,XD2
      COMMON/SIX/GP,G,GY,GX,GXX
      COMMON/FOUF/FRT,DFDX,DFDR1
    1 X=T/TCRT
      S=DEN/DCRT
       DSDR = DTRP/DCRT
    2 R=DEN/DTRP
      R2=R**2
      R3=R**3
    3 XB = PHIF(T)
        XC = 1/X
    4 XD = PSIF(T,DEN)
        XDD = DPSIDR
    6 A = A1 + A2*R + A3*R2 + A4*R3
       AD = A2 + 2*A3*R + 3*A4*R2
    7 B = B1 + B2*R + B3*R2
       BD = B2 + 2*B3*R
    8 C = C1*R + C2*R2 + C3*R3
       CD = C1 + 2*C2*R + 3*C3*R2
   10 U = S-1
      U1 = DSDR
   11 V = D1 + D2*R + D3*R2
      V1 = D2 + 2*D3*R
   14 D = U*V
       DD = U*V1 + U1*V
        F = A + B*XB + C*XC + D*XD
   16 DFDR = AD + BD*XB + CD*XC  +  D*XDD + DD*XD
   17 G = 1 + (R2*DFDR + 2*R*F)/X
      G1=G-1
      GY=1.0D0-G
      GX=DLOG(S)
      GXX=S-1
      GXS=DLOG(S)
      G=1+P*R/X
       DLPDLR = G/G
   20 DPDRF = DEN*GK*T*G
      GP=DPDRF*DLPDLR/DEN
      DFDR1=DFDR
        RETURN
       END
      FUNCTION DENGAS(T)
C     METHANE VAPOR DENSITIES VIA GOODWIN
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(5)
      DATA A / -7.169797, -1.705077, 1.461998, 0.416246, 0.524880/
      DATA   TTRP/90.68/,  TCRT/190.53/,  DCRT/10.15/
    1 U= (TCRT-T)/(TCRT-TTRP)
       W= (TCRT/T-1)/(TCRT/TTRP-1)
    3 F = A(1)*W + A(2)*U**0.36
```

```
   DO 4 K=3,5
4 F = F + A(K)*U**(K-2)
9 DENGAS = DCRT*DEXP(F)
  RETURN
  END
```

```
C     NBS PROGRAM TO GENERATE THE THERMODYNAMIC SURFACE FOR WATER
C     MAIN PROGRAM
      BLOCK DATA
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL P,G
      COMMON/ACONST/WM,GASCON,TZ,AA,ZB,DZB,YB,UREF,SREF
      COMMON/NCONST/G(40),II(40),JJ(40),NC
      COMMON/ELLCON/G1,G2,GF,B1,B2,B1T,B2T,B1TT,B2TT
      COMMON/BCONST/P(10),G(10)
      COMMON/ADDCON/ATZ(4),ADZ(4),AAT(4),AAD(4)
      DATA ATZ/2*64.D1,641.6D0,27.D1/,ADZ/3*.319D0,1.55D0/,AAT/2*2.D4
     $,4.D4,25.D0/,AAD/34.D0,4.D1,3.D1,1.05D3/
      DATA WM/18.0152D0/,GASCON/.461522D0/,TZ/647.073D0/,AA/1.D0/,NC/36/
      DATA UREF,SREF/-4328.455039D0,7.6180802D0/
      DATA G1,G2,GF/11.D0,44.3333333333333D0,3.5D0/
      DATA P/.7478629,-.3540782,2*0.,.007159876,0.,-.003528426,3*0./
      DATA G/1.1278334,0.,-.5944001,-5.010996,0.,.63684256,4*0./
      DATA G/-.5306296852902 3D3,.2274490142440 8D4,.7877933020687D3
     $,-.6983052737494 2D2,.1786383287542 2D5,-.3951473156333 8D5
     $,.3380388428075 3D5,-.1385505020270 3D5,-.2563743661326 0D6
     $,.4321257598 1415D6,-.3418301696966 0D6,.1222315641744 8D6
     $,.1177743655832D7,-.2173481011037 3D7,.1082995216862 0D7
     $,-.2544199806404 9D6,-.3137777494776 7D7,.5291910757704 7D7
     $,-.1380257717787 7D7,-.2510991436900 1D6,.4656182611560 8D7
     $,-.7275277327538 7D7,.4177424614829 4D6,.1401635824461 4D7
     $,-.3155523139212 7D7,.4792966638458 4D7,.4091266478 1209D6
     $,-.1362369738838 6D7,.6962522086266 4D6,-.1083490009764 47D7
     $,-.2272282740168 8D6,.3836548600660 6D6,.6883325794433 2D4
     $,.2175724552264 4D5,-.2662794482977 0D4,-.7073041808 2074D5
     $,-.225D0,-1.68D0,.055D0,-93.0D0/
      DATA II/4*0,4*1,4*2,4*3,4*4,4*5,4*6,4*8,2*2,0,4,3*2,4/
      DATA JJ/2,3,5,7,2,3,5,7,2,3,5,7,2,3,5,7,2,3,5,7,2,3,5,7,2,3,5,7
     $,2,3,5,7,1,3*4,0,2,0,0/
      END
      SUBROUTINE BB(T)
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL P,G
      COMMON/ELLCON/G1,G2,GF,B1,B2,B1T,B2T,B1TT,B2TT
      COMMON/ACONST/WM,GASCON,TZ,AA,Z,DZ,Y,UREF,SREF
      COMMON/BCONST/P(10),G(10)
      DIMENSION V(10)
      V(1)=1.
      DO 2 I=2,10
    2 V(I)=V(I-1)*TZ/T
      B1=P(1)+P(2)*DLOG(1./V(2))
      B2=G(1)
      B1T=P(2)*V(2)/TZ
      B2T=0.
      B1TT=0.
      B2TT=0.
      DO 4 I=3,10
      B1=B1+P(I)*V(I-1)
      B2=B2+G(I)*V(I-1)
      B1T=B1T-(I-2)*P(I)*V(I-1)/T
      B2T=B2T-(I-2)*G(I)*V(I-1)/T
      B1TT=B1TT+P(I)*(I-2)**2*V(I-1)/T/T
    4 B2TT=B2TT+G(I)*(I-2)**2*V(I-1)/T/T
      B1TT=B1TT-B1T/T
      B2TT=B2TT-B2T/T
      RETURN
```

```
      END
      SUBROUTINE BASE(D,T)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/ELLCON/G1,G2,GF,B1,B2,B1T,B2T,B1TT,B2TT
      COMMON/BASEF/AB,GB,SB,UB,HB,CVB,DPDTB
      COMMON/ACONST/WM,GASCON,TZ,A,Z,DZ,Y,UREF,SREF
      Y=.25*B1*D
      X=1. -Y
      ZO=(1. +G1*Y+G2*Y*Y)/X**3
      Z=ZO+4. *Y*(B2/B1-GF)
      DZO=(G1+2. *G2*Y)/X**3+3. *(1. +G1*Y+G2*Y*Y)/X**4
      DZ=DZO+4. *(B2/B1-GF)
      AB=-DLOG(X)-(G2-1. )/X+28. 16666667DO/X/X+4. *Y*(B2/B1-GF)
     $+15. 166666667DO+DLOG(D*T*4. 55483DO)
      GB=AB+Z
      BB2TT=T*T*B2TT
      UB=-T*B1T*(Z-1. -D*B2)/B1-D*T*B2T
      HB=Z+UB
      CVB=2. *UB+(ZO-1. )*((T*B1T/B1)**2-T*T*B1TT/B1)
     $-D*(BB2TT-GF*B1TT*T*T)-(T*B1T/B1)**2*Y*DZO
      DPDTB=Z/T+D*(DZ*B1T/4. +B2T-B2/B1*B1T)
      SB=UB-AB
      RETURN
      END
      SUBROUTINE GG(T,D)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/RESF/AR,GR,SR,UR,HR,CVR,DPDTR
      COMMON/GGGG/G,G5
      DIMENSION GR(11),GT(10),GZR(9),GZT(9)
      EQUIVALENCE (GR(3),GZR(1)),(GT(2),GZT(1))
      COMMON/NCONST/G(40),II(40),JJ(40),N
      COMMON/ACONST/WM,GASCON,TZ,AA,Z,DZ,Y,UREF,SREF
      COMMON/ADDCON/ATZ(4),ADZ(4),AAT(4),AAD(4)
      RT=GASCON*T
      GR(1)=0.
      G5=0.
      G=0. DO
      AR=0. DO
      DADT=0.
      CVR=0.
      DPDTR=0.
      E=DEXP(-AA*D)
      G10=D*D*E
      G20=1. DO-E
      GR(2)=G10
      V=TZ/T
      GT(1)=T/TZ
      DO 4 I=2,10
      GR(I+1)=GR(I)*G20
    4 GT(I)=GT(I-1)*V
      DO 10 I=1,N
      K=II(I)+1
      L=JJ(I)
      ZZ=K
      GP=G(I)*AA*GZR(K-1)*GZT(L)
      G=G+GP
      G5=G5+AA*(2. /D-AA*(1. -E*(K-1)/G20))*GP
      AR=AR+G(I)*GZR(K)*GZT(L)/G10/ZZ/RT
      DFDT=G20**K*(1-L)*GZT(L+1)/TZ/K
      D2F=L*DFDT
```

```
      DPT=DFDT*G10*AA*K/G20
      DADT=DADT+G(1)*DFDT
      DPDTR=DPDTR+G(I)*DPT
   10 CVR=CVR+G(I)*D2F/GASCON
      GP=0.
      G2A=0.
      DO 20 J=37, 40
      IF(G(J). EQ. 0. DO) GO TO 20
      K=II(J)
      KM=JJ(J)
      DDZ=ADZ(J-36)
      DEL=D/DDZ-1.
      IF(DABS(DEL). LT. 1. D-10) DEL=1. D-10
      DD=DEL*DEL
      EX1=-AAD(J-36)*DEL**K
      DEX=DEXP(EX1)*DEL**KM
      ATT=AAT(J-36)
      TX=ATZ(J-36)
      TAU=T/TX-1.
      EX2=-ATT*TAU*TAU
      TEX=DEXP(EX2)
      G10=DEX*TEX
      GM=KM/DEL-K*AAD(J-36)*DEL**(K-1)
      FCT=GM*D**2*G10/DDZ
      G5T=FCT*(2. /D+GM/DDZ)-(D/DDZ)**2*G10*(KM/DEL/DEL+
     $K*(K-1)*AAD(J-36)*DEL**(K-2))
      G5=G5+G5T*G(J)
      GP=GP+G(J)*FCT
      DADT=DADT-2. *G(J)*ATT*TAU*G10/TX
      DPDTR=DPDTR-2. *G(J)*ATT*TAU*FCT/TX
      G2A=G2A+T*G(J)*(4. *ATT*EX2+2. *ATT)*G10/TX/TX
      AR=AR+G10*G(J)/RT
   20 CONTINUE
      SR=-DADT/GASCON
      UR=AR+SR
      CVR=CVR+G2A/GASCON
      G=G+GP
      RETURN
      END
      SUBROUTINE DFIND(DOUT, P, D, T, DPD)
      IMPLICIT REAL*8 (A-H, O-Z)
      COMMON/GGGG/GO, G5
      COMMON/ACONST/WM, GASCON, TZ, AA, Z, DZ, Y, UREF, SREF
      DD=D
      RT=GASCON*T
      IF(DD. LE. 0. ) DD=1. D-8
      IF(DD. GT. 1. 9) DD=1. 9
      L=0
    9 L=L+1
   11 IF(DD. LE. 0) DD=1. D-8
      IF(DD. GT. 1. 9) DD=1. 9
      CALL BASE(DD, T)
      CALL GG(T, DD)
      PP=RT*DD*Z+GO
      DPD=RT*(Z+Y*DZ)+G5
      IF(DPD. GT. 0. DO) GO TO 13
      IF(D. GE. . 2967D0) DD=DD*1. 02D0
      IF(D. LT. . 2967D0) DD=DD*. 98D0
      IF(L. LE. 10) GO TO 9
   13 DPDX=DPD*1. 1
```

```
      IF(DPDX.LT..1) DPDX=.1
      DP=DABS(1.-PP/P)
      IF(DP.LT.1.D-8) GO TO 20
      IF(D.GT..3 .AND. DP.LT.1.D-7) GO TO 20
      IF(D.GT..7 .AND. DP.LT.1.D-6) GO TO 20
      X=(P-PP)/DPDX
      IF(DABS(X).GT..1) X=X*.1/DABS(X)
      DD=DD+X
      IF(DD.LE.0.) DD=1.D-8
   19 IF(L.LE.30) GO TO 9
   20 CONTINUE
      DOUT=DD
      RETURN
      END
      SUBROUTINE THERM(D,T)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/ACONST/WM,GASCON,TZ,AA,ZB,DZB,Y,UREF,SREF
      COMMON/GGGG/GP,GDP
      COMMON/BASEF/AB,GB,SB,UB,HB,CVB,DPDTB
      COMMON/RESF/AR,GR,SR,UR,HR,CVR,DPDTR
      COMMON/IDF/AI,GI,SI,UI,HI,CVI,CPI
      COMMON/FCTS/AD,GD,SD,UD,HD,CVD,CPD,DPDT,DVDT,CJTT,CJTH
      CALL IDEAL(T)
      RT=GASCON*T
      Z=ZB+GP/RT/D
      DPDD=RT*(ZB+Y*DZB)+GDP
      AD=AB+AR+AI-UREF/T+SREF
      GD=AD+Z
      UD=UB+UR+UI-UREF/T
      DPDT=RT*D*DPDTB+DPDTR
      CVD=CVB+CVR+CVI
      CPD=CVD+T*DPDT**2/(D*D*DPDD*GASCON)
      HD=UD+Z
      SD=SB+SR+SI-SREF
      DVDT=DPDT/DPDD/D/D
      CJTT=1./D-T*DVDT
      CJTH=-CJTT/CPD/GASCON
      RETURN
      END
      FUNCTION PS(T)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(8)
      DATA A/-7.8889166D0,2.5514255D0,-6.716169D0
     $,33.239495D0,-105.38479D0,174.35319D0,-148.39348D0
     $,48.631602D0/
      IF(T.GT.314.D0) GO TO 2
      PL=6.3573118D0-8858.843D0/T+607.56335D0*T**(-.6)
      PS=.1*DEXP(PL)
      RETURN
    2 V=T/647.25D0
      W=DABS(1.D0-V)
      B=0.D0
      DO 4 I=1,8
      Z=I
    4 B=B+A(I)*W**((Z+1.)/2.)
      G=B/V
      PS=22.093D0*DEXP(G)
      RETURN
      END
      FUNCTION TSAT(P)
```

```
      REAL*8 P,PS,TG,TSAT,TDPSDT
      TSAT=0.
      IF(P.GT.22.05) RETURN
      K=0
      PL=2.302585*DLOG(P)
      TG=372.83+PL*(27.7589+PL*(2.3819+PL*(.24834+PL*.0193855)))
    1 IF(TG.LT.273.15) TG=273.15
      IF(TG.GT.647.) TG=647.
      IF(K.LT.8) GO TO 2
      WRITE(6,3) K,P,PP,TG
    3 FORMAT()
      GO TO 8
    2 K=K+1
      PP=PS(TG)
      DP=TDPSDT(TG)
      IF(DABS(1.-PP/P).LT..00001) GO TO 8
      TG=TG*(1.+(P-PP)/DP)
      GO TO 1
    8 TSAT=TG
      RETURN
      END
      FUNCTION TDPSDT(T)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(8)
      DATA A/-7.8889166D0,2.5514255D0,-6.716169D0
     *,33.239495D0,-105.38479D0,174.35319D0,-148.39348D0
     *,48.631602D0/
      V=T/647.25
      W=1.-V
      B=0.
      C=0.
      DO 4 I=1,8
      Z=I
      Y=A(I)*W**((Z+1.)/2.)
      C=C+Y/W*(.5-.5*Z-1./V)
    4 B=B+Y
      Q=B/V
      TDPSDT=22.093*DEXP(Q)*C
      RETURN
      END
      SUBROUTINE IDEAL(T)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/IDF/AI,GI,SI,UI,HI,CVI,CPI
      DIMENSION C(18)
      DATA C/.19730271018D2,.209662681977D2,-.483429455355D0
     *,.605743189245D1,22.56023885D0,-9.87532442D0,-.43135538513D1
     *,.45815578ID0,-.47754901883D-1,.412384606333D-2,-.27929052852D-3
     *,.14481695261D-4,-.56473658748D-6,.16200446D-7,-.3303822796D-9
     *,.45191606736BD-11,-.370734122708D-13,.137546068238D-15/
      TT=T/1.D2
      TL=DLOG(TT)
      GI=-(C(I)/TT+C(2))*TL
      HI=(C(2)+C(1)*(1.D0-TL)/TT)
      CPI=C(2)-C(1)/TT
      DO 8 I=3,18
      GI=GI-C(I)*TT**(I-6)
      HI=HI+C(I)*(I-6)*TT**(I-6)
    8 CPI=CPI+C(I)*(I-6)*(I-5)*TT**(I-6)
      AI=GI-1
      UI=HI-1
```

```
      CVI=CPI-1
      SI=UI-AI
      RETURN
      END
      SUBROUTINE SECVIR(T,VIR)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/NCONST/G(40),II(40),JJ(40),NC
      COMMON/ELLCON/G1,G2,GF,BB1,BB2,B1T,B2T,B1TT,B2TT
      COMMON/GGGG/GO,GS
      COMMON/ACONST/WM,GASCON,TC,AA,Z,DZ,Y,UREF,SREF
      CALL BB(T)
      V=TC/T
      VIR=BB2
      DO 3 J=1,NC
      IF(II(J).NE.0) GO TO 3
      L=JJ(J)
      VIR=VIR+G(J)*V**(L-1)/T/GASCON
    3 CONTINUE
      RETURN
      END
      SUBROUTINE CORR(T,P,DL,DV,DELG)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/GGGG/GOO,G11
      COMMON/ACONST/WM,GASCON,TZ,AA,ZB,DZB,YB,UREF,SREF
      COMMON/FCTS/AD,GD,SD,UD,HD,CVD,CPD,DPDT,DVDT,CJTT,CJ
      DLIQ=DL
      IF(DL.LE.0.) DLIQ=1.11-.0004*T
      CALL BB(T)
      RT=GASCON*T
      CALL DFIND(DL,P,DLIQ,T,DQ)
      CALL THERM(DL,T)
      GL=GD
      DVAP=DV
      IF(DV.LE.0.) DVAP=P/GASCON/T
      CALL DFIND(DV,P,DVAP,T,DQ)
      IF(DV.LT.5.D-7) DV=5.D-7
      CALL THERM(DV,T)
      GV=GD
      DELG=GL-GV
      RETURN
      END
      SUBROUTINE PCORR(T,P,DL,DV)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/ACONST/WM,GASCON,TZ,AA,ZB,DZB,YB,UREF,SREF
      P=PS(T)
    2 CALL CORR(T,P,DL,DV,DELG)
      DP=DELG*GASCON*T/(1./DV-1./DL)
      P=P+DP
      IF(DABS(DELG).LT.1.D-4) RETURN
      GO TO 2
      END
      SUBROUTINE TCORR(T,P,DL,DV)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON/ACONST/WM,GASCON,TZ,AA,ZB,DZB,YB,UREF,SREF
      T=TSAT(P)
    2 CALL CORR(T,P,DL,DV,DELG)
      DP=DELG*GASCON*T/(1./DV-1./DL)
      T=T*(1.-DP/TDPSDT(T))
      IF(DABS(DELG).LT.1.D-4) RETURN
      GO TO 2
```

```
      END
      SUBROUTINE UNIT
      IMPLICIT REAL*8 (A-H,O-Z)
      DOUBLE PRECISION NT,ND,NP,NH,NNT,NND,NNP,NNH
      COMMON/UNITS/IT,ID,IP,IH,NT,ND,NP,NH,FT,FD,FP,FH
      DIMENSION FFD(4),FFP(5),FFH(6),NNT(4),NND(4),NNP(5),NNH(6)
      DATA FFD/1.D-3,1.D0,.0180152D0,.01601BD0/
      DATA FFP/1.D0,10.D0,9.869232667D0,145.038D0,10.1971D0/
      DATA FFH/2*1.D0,18.0152D0,.23884590D0,4.30285666D0,.42D0/
      DATA NNT/1HK,1HC,1HR,1HF/
      DATA NND/6HKG/M3 ,6HG/CM3 ,6HMOL/L ,6HLB/FT3/
      DATA NNP/6H MPA  ,6H BAR  ,6H ATM  ,6H PSI  ,6HKG/CM2/
      DATA NNH/6HKJ/KG ,6H J/G  ,6HJ/MOL ,6HCAL/G ,7HCAL/MOL,6HBTU/LB/
      DATA A1,A2,A3,A4/8HTEMPERAT,7HDENSITY
     *,8HPRESSURE,8HENERGY    /
      WRITE(6,11) A1
   30 WRITE(6,12)
      READ(5,*,END=99) IT
      IF(IT.EQ.0) STOP
      IF(IT.GT.4) GO TO 30
      NT=NNT(IT)
      WRITE(6,11) A2
   31 WRITE(6,13)
      READ(5,*,END=99) ID
      IF(ID.GT.4 .OR. ID.LT.1) GO TO 31
      ND=NND(ID)
      FD=FFD(ID)
      WRITE(6,11) A3
   32 WRITE(6,14)
      READ(5,*,END=99) IP
      IF(IP.GT.5 .OR. IP.LT.1) GO TO 32
      NP=NNP(IP)
      FP=FFP(IP)
      WRITE(6,11) A4
   33 WRITE(6,15)
      READ(5,*,END=99) IH
      IF(IH.GT.6 .OR. IH.LT.1) GO TO 33
      NH=NNH(IH)
      FH=FFH(IH)
      RETURN
   99 STOP
   11 FORMAT(' ENTER UNITS CHOSEN FOR ',A8)
   12 FORMAT(' CHOOSE FROM 1=DEG K, 2=DEG C, 3=DEG R, 4=DEG F')
   13 FORMAT(' CHOOSE FROM 1=KG/M3, 2=G/CM3, 3=MOL/L, 4=LB/FT3')
   14 FORMAT(' CHOOSE FROM 1=MPA, 2=BAR, 3=ATM, 4=PSIA, 5=KG/CM2')
   15 FORMAT(' CHOOSE FROM 1=KJ/KG, 2=J/G, 3=J/MOL, 4=CALORI
     $ES/MOL, 6=BTU/LB')
      END
      FUNCTION TTT(T)
      DOUBLE PRECISION T,TTT,FT,FD,FP,FH,NT,ND,NP,NH
      COMMON/UNITS/IT,ID,IP,IH,NT,ND,NP,NH,FT,FD,FP,FH
      GO TO (1,2,3,4),IT
    1 TTT=T
      FT=1.
      RETURN
    2 TTT=T+273.15D0
      FT=1.
      RETURN
    3 TTT=T/1.8D0
      FT=.5555555555556D0
```

```
      RETURN
    4 TTT=(T+459.67D0)/1.8D0
      FT=.5555555555556D0
      RETURN
      END
      FUNCTION TTI(T)
      DOUBLE PRECISION T,TTI,FT,FD,FP,FH,NT,ND,NP,NH
      COMMON/UNITS/IT,ID,IP,IH,NT,ND,NP,NH,FT,FD,FP,FH
      GO TO (5,6,7,8),IT
    5 TTI=T
      RETURN
    6 TTI=T-273.15D0
      RETURN
    7 TTI=T*1.8D0
      RETURN
    8 TTI=T*1.8D0-459.67D0
      RETURN
      END
C     MAIN(H20)
      IMPLICIT REAL*8 (A-H,O-Z)
      DOUBLE PRECISION NT,ND,NP,NH
      COMMON/UNITS/IT,ID,IP,IH,NT,ND,NP,NH,FT,FD,FP,FH
      COMMON/GGGG/GO,G5
      COMMON/FCTS/AD,GD,SD,UD,HD,CVD,CPD,DPDT
      COMMON/ACONST/WM,GASCON,TC,AA,Z,DZ,Y,UREF,SREF
      COMMON/NCONST/G(40),II(40),JJ(40),NC
      DATA NS1,NS2/2H M,2HFT/
      CALL UNIT
      NS=NS1
      IF(ID.EQ.4) NS=NS2
   15 READ(5,*,END=9) IOPT,XISO
      IF(IOPT.EQ.0) GO TO 9
      GO TO (101,201,301),IOPT
  101 READ(5,*,END=9) JOPT,Y1,Y2,YI
      IF(JOPT-1) 15,101,103
  103 TT=XISO
      T=TTT(TT)
      IF(JOPT.EQ.2) DGSS=Y1/FP/T/.4
      IZ=0
      CALL BB(T)
      PSS=20000.
      DVV=0.
      IF(T.LT.TC) CALL PCORR(T,PSS,DLL,DVV)
      DGSS=DVV
      IF(DGSS.EQ.0.) DGSS=1.11-.0004*T
      PSAT=PSS*FP
      IF(JOPT.EQ.2 .AND. Y1.GT.PSAT) IZ=3
      IF(Y1.GT.PSAT) DGSS=DLL
      IF(JOPT.GE.3) IZ=3
      PIN=Y1-YI
      DIN=PIN
      PINC=YI/FP
      DINC=YI*FD
   22 IF(JOPT.EQ.2) PIN=PIN+YI
      IF(JOPT.EQ.3) DIN=DIN+YI
      IF(JOPT.EQ.2 .AND. PIN.GT.Y2) GO TO 101
      IF(JOPT.EQ.3 .AND. DIN.GT.Y2) GO TO 101
      IF(JOPT.EQ.2) PRES=PIN/FP
      IF(JOPT.EQ.3) D=DIN/FD
   24 CONTINUE
```

```
      IF(JOPT.EQ.3 .OR. (JOPT.EQ.2 .AND. PIN.LT.PSAT)) GO TO 26
      IF(JOPT.EQ.1 .AND. T.LT.TS) GO TO 26
      TSAVE=TT-YI
      IF(JOPT.EQ.1 .AND. IOPT.EQ.2 .AND. IZ.LE.2) TT=TTI(TS)
      PSAVE=PIN-YI
      IF(JOPT.EQ.2 .AND. PRES.GT.PSAT/FP .AND. IZ.GE.2) GO TO 26
      IF(JOPT.EQ.1 .AND. T.GT.TS .AND. IZ.GE.2) GO TO 26
   23 IZ=IZ+1
      IF(JOPT.EQ.2) PRES=PSAT/FP
      IF(JOPT.EQ.1) T=TS
      IF(IZ.EQ.1 .AND. JOPT.EQ.1) DQSS=DLL
      IF(IZ.EQ.1 .AND. JOPT.EQ.2) DQSS=DVV
      IF(IZ.EQ.2 .AND. JOPT.EQ.2) DQSS=DLL
      IF(IZ.EQ.2 .AND. JOPT.EQ.1) DQSS=DVV
      CALL BB(T)
   26 IF(IOPT.NE.3 .AND. JOPT.NE.3) CALL DFIND(D,PRES,DQSS,T,DQ)
   27 CALL GQ(T,D)
      CALL BASE(D,T)
      RT=GASCON*T
      PDUM=D*RT*Z+GQ
      IF(JOPT.EQ.3 .OR. JOPT.EQ.3) PRES=PDUM
      IF(IOPT.EQ.3 .OR. JOPT.EQ.3) DQ=RT*(Z+Y*DZ)+GS
      DQSS=D+PINC/DQ
      CALL THERM(D,T)
      U=UD*T*GASCON*FH
      C=DSQRT(DABS(CPD*DQ*1.D3/CVD))
      IF(ID.EQ.4) C=C*3.280833
      H=HD*T*GASCON*FH
      S=SD*GASCON*FH*FT
      DPDTX=DPDT*FP*FT
      DPDD=DQ*FP*FD
      COMP=1.D3/D/DQ/FP
      DDDTL=-1.D3*DPDT/D/DQ
      CP=CPD*GASCON*FH*FT
      CV=CVD*GASCON*FH*FT
      VL=FD/D
      DOUT=1.0D03*VL
      POUT=PRES*FP
      ROUT=DOUT/17.857142D0
      XOUT=ROUT-1.D0
      GP=DPDD/0.0831434D0/TT
      GP1=1.D0-GP
      WRITE(6,21) TT,POUT,DOUT,GP1
   21 FORMAT(F9.3,3F12.5)
      IF(IZ.EQ.1) WRITE(6,12)
   12 FORMAT('  ------------------------------------------------------------
     $----------------------')
      IF(IZ.EQ.1) GO TO 23
      IF(IZ.EQ.2 .AND. JOPT.EQ.2) PIN=PSAVE
      IF(IZ.EQ.2 .AND. JOPT.EQ.1) TT=TSAVE
      IF(IZ.EQ.2) IZ=3
      GO TO (22,204,304),IOPT
  201 JOPT=1
      PRES=XISO/FP
  202 READ(5,*,END=9) T1,T2,YI
      IF(T1.EQ.0.) GO TO 15
      TT=T1-YI
      T=TTT(TT)
      CALL TCORR(TS,PRES,DLL,DVV)
      D=DLL
```

```
      IF((T+YI*FT).LT.TS) IZ=0
  204 TT=TT+YI
      T=TTT(TT)
      IF(TT.GT.T2) GO TO 202
      CALL BB(T)
      DGSS=D
      GO TO 24
  301 JOPT=1
      D=XISD
  302 READ(5,*,END=9) T1,T2,YI
      IF(T1.LE.0.) GO TO 15
      TT=T1-YI
      IZ=3
      T=TTT(T)
  304 TT=TT+YI
      T=TTT(TT)
      IF(TT.GT.T2) GO TO 302
      CALL BB(T)
      GO TO 27
    9 STOP
      END
```

```
C      CORRESPONDING STATES CORRELATION OF THE DIRECT
C      CORRELATION FUNCTION INTEGRALS OF PURE LIQUIDS
C      MAIN PROGRAM
       IMPLICIT REAL*8(A-H,O-Z)
       DIMENSION P(4),STEP(4),AB(4),BB(4),NAME(20)
       DIMENSION TEMP(22),TR(22),DR(8),RRHO(8),DEXP(8),
      1DCAL(8),DEV(8),ERR(8)
       DIMENSION VI(8,22),CI(8,22),PI(8,22),PII(8),
      1PRES(8),V(8),VII(8),CII(8)
       COMMON/DATA/TEMP,VI,CI,DEXP,DCAL,VC
       COMMON/COND/NP,NJ,NN,TERM
       COMMON/PRINT/DDEX(8,22),DDCA(8,22)
       COMMON/PARAM/RHOS,DCFS,TS
       READ(5,1) NAME
     1 FORMAT(20A4)
       READ(5,3) NJ
     3 FORMAT(I2)
       WRITE(6,4) NJ
     4 FORMAT(1X,'NO. OF ISOTHERMS= ',I2,//)
       READ(5,20) NP,IO
    20 FORMAT(2I2)
       READ(5,7) NPASS,(P(I),I=1,NP),(STEP(I),I=1,NP)
       READ(5,8) (AB(I),I=1,NP),(BB(I),I=1,NP)
     7 FORMAT(I2,6F10.0)
     8 FORMAT(3X,6F10.0)
       WRITE(6,101)
   101 FORMAT(1X,'PATTERN SEARCH ESTIMATION OF PARAMETERS FROM
      1DCFI DATA'/1X,'CONTROL PARAMETERS WERE SET AS FOLLOWS-'/)
       WRITE(6,102) NP,IO
   102 FORMAT(1X,5H  NP=,I2/1X,5H  IO=,I2)
       WRITE(6,106) NPASS
   106 FORMAT(1X,15HNUMBER OF PASS=,I2)
       WRITE(6,107)
   107 FORMAT(1X,18HINITIAL PARAMETERS)
       WRITE(6,108) (I,P(I),I=1,NP)
   108 FORMAT(1X,I2,F10.3)
       WRITE(6,109)
   109 FORMAT(1X,12HSIZE OF STEP)
       WRITE(6,110) (I,STEP(I),I=1,NP)
   110 FORMAT(1X,I2,F10.3)
       WRITE(6,111)
   111 FORMAT(1X,30HLOWER LIMITS OF THE PARAMETERS)
       WRITE(6,112) (I,AB(I),I=1,NP)
   112 FORMAT(1X,I2,F10.3)
       WRITE(6,113)
   113 FORMAT(1X,30HUPPER LIMITS OF THE PARAMETERS)
       WRITE(6,114) (I,BB(I),I=1,NP)
   114 FORMAT(1X,I2,F10.3)
       READ(5,120) TC,VC
   120 FORMAT(2F10.0)
       DO 200 II=1,NJ
       READ(5,300) TEMP(II)
       READ(5,300) VII,CII,PII
   300 FORMAT(8F10.0)
       DO 400 KK=1,8
       VI(KK,II)=VII(KK)
       CI(KK,II)=CII(KK)
       PI(KK,II)=PII(KK)
   400 CONTINUE
   200 CONTINUE
```

```
      CALL PATERN(NP,P,STEP,NPASS,2,AB,BB)
      CALL DCFI(P,SUM)
      WRITE(6,202) NAME
  202 FORMAT(////20H  THE SUBSTANCE IS : 20A4//)
      WRITE(6,130) TC,VC,TS,RHOS,DCFS
  130 FORMAT(//'  TC=',F8.3,' K'//'  VC=',
     1F8.3,  ' CC/GMOL'//'  T*=',
     1F8.3,' K'//'  D*=',F8.4,' GMOL/L'//'  C*=',F9.4//)
      TOT=0.0D0
      DO 116 J=1,NJ
      TR(J)=TEMP(J)/TS
      WRITE(6,117) TEMP(J),TR(J)
  117 FORMAT(//1X,'FOR THE ISOTHERM AT',  F7.2,  ' DEG.  K,',
     1'THE REDUCED TEMPERATURE IS',F7.4//)
      WRITE(6,115)
  115 FORMAT(2X,3HNO. ,3X,5HP,BAR,3X,8HV,CC/MOL,5X,4HD/D*,4X,
     15HC,EXP,5X,5HC,CAL,7X,4HDEV. ,5X,5H% ERR/)
      DO 118 I=1,8
      PRES(I)=PI(I,J)
      V(I)=VI(I,J)
      DEXP(I)=DDEX(I,J)
      DCAL(I)=DDCA(I,J)
      IF(DABS(DEXP(I)).LT.1.0D-5) GO TO 118
      DEV(I)=DEXP(I)-DCAL(I)
      ERR(I)=DEV(I)/DEXP(I)*100.D0
      TOT=TOT+DABS(ERR(I))
      DR(I)=VC/V(I)
      RRHO(I)=1.0D03/VI(I,J)/RHOS
      WRITE(6,119) I,PRES(I),V(I),RRHO(I),DEXP(I),
     1DCAL(I),DEV(I),ERR(I)
  119 FORMAT(1X,I3,F10.2,7F10.4)
  118 CONTINUE
  116 CONTINUE
      AVG=TOT/TERM
      WRITE(6,201) AVG
  201 FORMAT(//30H AVERAGE PERCENTAGE ERROR IS =,F10.4//)
      STOP
      END
      SUBROUTINE PATERN(NP,P,STEP,NPASS,IO,AB,BB)
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      DIMENSION P(NP),STEP(NP)
      DIMENSION B1(4),B2(4),T(4),S(4),AB(4),BB(4)
      IOF=6
      NRD=NPASS
      L=1
      ICK=2
      ITTER=0
      DO 5 I=1,NP
      B1(I)=P(I)
      B2(I)=P(I)
      T(I)=P(I)
    5 S(I)=STEP(I)*10.
      CALL BOUNDS(P,IOUT,AB,BB,NP)
      IF(IOUT.LE.0) GO TO 10
      IF(IO.LE.0) GO TO 6
      WRITE(IOF,1005)
      WRITE(IOF,1000)(J,P(J),J=1,NP)
    6 GO TO 999
   10 CALL DCFI(P,C1)
      IF(IO.LE.1) GO TO 11
```

```
      WRITE(IOF,1001) ITTER,C1
      WRITE(IOF,1000) (J,P(J),J=1,NP)
   11 DO 99 INRD=1,NRD
      DO 12 I=1,NP
   12 S(I)=S(I)/10.
      IF(IO.LE.1) GO TO 20
      WRITE(IOF,1003)
      WRITE(IOF,1000) (J,S(J),J=1,NP)
   20 IFAIL=0
      DO 30 I=1,NP
      IC=0
   21 P(I)=T(I)+S(I)
      IC=IC+1
      CALL BOUNDS(P,IOUT,AB,BB,NP)
      IF(IOUT.GT.0) GO TO 23
      CALL DCFI(P,C2)
      L=L+1
      IF(IO.LT.3) GO TO 22
      WRITE(IOF,1002) L,C2
      WRITE(IOF,1000) (J,P(J),J=1,NP)
   22 IF(C1-C2) 23,23,25
   23 IF(IC.GE.2) GO TO 24
      S(I)=-S(I)
      GO TO 21
   24 IFAIL=IFAIL+1
      P(I)=T(I)
      GO TO 30
   25 T(I)=P(I)
      C1=C2
   30 CONTINUE
      IF(IFAIL.LT.NP) GO TO 35
      IF(ICK.EQ.2) GO TO 90
      IF(ICK.EQ.1) GO TO 35
      CALL DCFI(T,C2)
      L=L+1
      IF(IO.LT.3) GO TO 31
      WRITE(IOF,1002) L,C2
      WRITE(IOF,1000) (J,T(J),J=1,NP)
   31 IF(C1-C2) 32,34,34
   32 ICK=1
      DO 33 I=1,NP
      B1(I)=B2(I)
      P(I)=B2(I)
   33 T(I)=B2(I)
      GO TO 20
   34 C1=C2
   35 IB1=0
      DO 37 I=1,NP
      B2(I)=T(I)
      IF(DABS(B1(I)-B2(I)).LT.(DABS(S(I))*.01)) IB1=IB1+1
   37 CONTINUE
      IF(IB1.EQ.NP) GO TO 90
      ICK=0
      ITTER=ITTER+1
      IF(IO.LT.2) GO TO 40
      WRITE(IOF,1001) ITTER,C1
      WRITE(IOF,1000) (J,T(J),J=1,NP)
   40 SJ=1.
      DO 45 II=1,11
      DO 42 I=1,NP
```

```
      T(I)=B2(I)+SJ*(B2(I)-B1(I))
   42 P(I)=T(I)
      SJ=SJ-.1
      CALL BOUNDS(T,IOUT,AB,BB,NP)
      IF(IOUT.LT.1) GO TO 46
      IF(II.EQ.11) ICK=1
   45 CONTINUE
   46 DO 47 I=1,NP
   47 B1(I)=B2(I)
      GO TO 20
   90 DO 91 I=1,NP
   91 T(I)=B2(I)
   99 CONTINUE
      DO 100 I=1,NP
  100 P(I)=T(I)
      COST=C1
      IF(IO.LE.0) GO TO 999
      WRITE(IOF,1004) L,C1
      WRITE(IOF,1000) (J,P(J),J=1,NP)
  999 CONTINUE
      RETURN
 1000 FORMAT(1X,5(I7,E13.6)/)
 1001 FORMAT(//1X,13HITERATION NO.,I5/5X,5HCOST=,E15.6,20X,
     110HPARAMETERS)
 1002 FORMAT(10X,3HNO.,I4,8X,5HCOST=,E15.6)
 1003 FORMAT(/1X,28HSTEP SIZE FOR EACH PARAMETER)
 1004 FORMAT(1X,13HANSWERS AFTER,I3,2X,22HFUNCTIONAL EVALUATIONS
     1//5X,5HCOST=,E15.6,20X,18HOPTIMAL PARAMETERS)
 1005 FORMAT(1X,35HINITIAL PARAMETERS OUT OF BOUNDS    )
      END
      SUBROUTINE BOUNDS(P,IOUT,AB,BB,NP)
      REAL*8 AB(4),BB(4),P(4)
      IOUT=0
      DO 1 I=1,NP
    1 IF(P(I).LE.AB(I) .OR.  P(I).GT.BB(I)) IOUT=1
      RETURN
      END
      SUBROUTINE DCFI(P,SUM)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION VI(8,22),CI(8,22),RHO(8)
      DIMENSION P(4),TEMP(22),DEXP(8),DCAL(8)
      COMMON/DATA/TEMP,VI,CI,DEXP,DCAL,VC
      COMMON/COND/NP,NJ,NN,TERM
      COMMON/PRINT/DDEX(8,22),DDCA(8,22)
      COMMON/PARAM/RHOS,DCFS,TS
      RHOS=P(1)
      DCFS=P(2)
      TS=P(3)
      SUM=0.0D0
      TERM=0.0D0
      DO 6 J=1,NJ
      TT=TS/TEMP(J)
      NN=0
      DO 10 K=1,8
      IF(VI(K,J).LT.1.0D0) GO TO 10
      NN=NN+1
      RHO(NN)=1.0D03/VI(K,J)
      DEXP(NN)=CI(K,J)
   10 CONTINUE
      DO 13 I=1,NN
```

```
      DN=RHO(I)/RHOS
      TERM=TERM+1
      A0=0.78642D01-0.10191D02*TT-0.15356D01*TT*TT
      A1=-0.28465D02+0.30864D02*TT+0.60294D01*TT*TT
      A2=0.27542D02-0.32898D02*TT-0.87130D01*TT*TT
      A3=-0.82606D01+0.12737D02*TT+0.4017OD01*TT*TT
      DCAL(I)=(A0+DN*(A1+DN*(A2+DN*A3)))*DCFS
      SUM=SUM+(DCAL(I)-DEXP(I))**2
      DDEX(I,J)=DEXP(I)
      DDCA(I,J)=DCAL(I)
   13 CONTINUE
    6 CONTINUE
      SUM=DSQRT(SUM/(TERM-1.0D0))
      RETURN
      END
```

```
C      CORRESPONDING STATES CORRELATION OF THE VOLUMETRIC
C      PROPERTIES OF COMPRESSED PURE LIQUIDS.
C      MAIN PROGRAM
       IMPLICIT REAL*8(A-H,O-Z)
       DIMENSION P(4),STEP(4),AB(4),BB(4),NAME(20)
       DIMENSION TEMP(34),TR(34),DR(8),RRHO(8),PEXP(8),
      1PCAL(8),DEV(8),ERR(8)
       DIMENSION VI(8,34),CI(8,34),PI(8,34),PII(8),
      1PRES(8),V(8),VII(8),CII(8)
       COMMON/DATA/TEMP,VI,PI,PEXP,PCAL,VC
       COMMON/COND/NP,NJ,NN,TERM
       COMMON/PRINT/PPEX(8,34),PPCA(8,34)
       COMMON/PARAM/RHOS,DCFS,TS
       READ(5,1) NAME
     1 FORMAT(20A4)
       READ(5,3) NJ
     3 FORMAT(I2)
       WRITE(6,4) NJ
     4 FORMAT(1X,'NO. OF ISOTHERMS= ',I2,//)
       READ(5,20) NP,IO
    20 FORMAT(2I2)
       READ(5,7) NPASS,(P(I),I=1,NP),(STEP(I),I=1,NP)
       READ(5,8) (AB(I),I=1,NP),(BB(I),I=1,NP)
     7 FORMAT(I2,6F10.0)
     8 FORMAT(3X,6F10.0)
       WRITE(6,101)
   101 FORMAT(1X,'PATTERN SEARCH ESTIMATION OF PARAMETERS FROM
      1 PVTX DATA'/1X,'CONTROL PARAMETERS WERE SET AS FOLLOWS-'/)
       WRITE(6,102) NP,IO
   102 FORMAT(1X,5H  NP=,I2/1X,5H  IO=,I2)
       WRITE(6,106) NPASS
   106 FORMAT(1X,15HNUMBER OF PASS=,I2)
       WRITE(6,107)
   107 FORMAT(1X,18HINITIAL PARAMETERS)
       WRITE(6,108) (I,P(I),I=1,NP)
   108 FORMAT(1X,I2,F10.3)
       WRITE(6,109)
   109 FORMAT(1X,12HSIZE OF STEP)
       WRITE(6,110) (I,STEP(I),I=1,NP)
   110 FORMAT(1X,I2,F10.3)
       WRITE(6,111)
   111 FORMAT(1X,30HLOWER LIMITS OF THE PARAMETERS)
       WRITE(6,112) (I,AB(I),I=1,NP)
   112 FORMAT(1X,I2,F10.3)
       WRITE(6,113)
   113 FORMAT(1X,30HUPPER LIMITS OF THE PARAMETERS)
       WRITE(6,114) (I,BB(I),I=1,NP)
   114 FORMAT(1X,I2,F10.3)
       READ(5,120) TC,VC
   120 FORMAT(2F10.0)
       DO 200 II=1,NJ
       READ(5,300) TEMP(II)
       READ(5,300) VII,CII,PII
   300 FORMAT(8F10.0)
       DO 400 KK=1,8
       VI(KK,II)=VII(KK)
       CI(KK,II)=CII(KK)
       PI(KK,II)=PII(KK)
   400 CONTINUE
   200 CONTINUE
```

```
      CALL PATERN(NP,P,STEP,NPASS,2,AB,BB)
      CALL DCFI(P,SUM)
      WRITE(6,202) NAME
202 FORMAT(////21H  THE SUBSTANCE IS : 20A4//)
      WRITE(6,130) TC,VC,TS,RHOS,DCFS
130 FORMAT(//'  TC=',F8.3,' K''  VC=',
     1F8.3,  ' CC/GMOL''  T*=',
     1F8.3,' K''  D*=',F8.4,' GMOL/L''  C*=',F9.4//)
      TOT=0.0D0
      DO 116 J=1,NJ
      TR(J)=TEMP(J)/TS
      WRITE(6,117) TEMP(J),TR(J)
117 FORMAT(//1X,'FOR THE ISOTHERM AT',  F7.2,  ' DEG.  K,',
     1'THE REDUCED TEMPERATURE IS',F7.4)
      WRITE(6,134) PI(1,J),  VI(1,J)
134 FORMAT(//1X,'THE REF.  PRESSURE IS',F9.4,  '
     1 BAR,',' THE REF.  MOLAR VOLUME IS',F9.4,  ' CC/GMOL'//)
      WRITE(6,115)
115 FORMAT(2X,3HNO. ,3X,5HP,BAR,3X,8HV,CC/MOL,5X,4HD/D*,4X,
     15HP,EXP,5X,5HP,CAL,7X,4HDEV. ,5X,5HZ  ERR/)
      DO 118 I=2,8
      PRES(I)=PI(I,J)
      V(I)=VI(I,J)
      PEXP(I)=PPEX(I,J)
      PCAL(I)=PPCA(I,J)
      IF(DABS(PEXP(I)).LT.1.0D-5) GO TO 118
      DEV(I)=PEXP(I)-PCAL(I)
      ERR(I)=DEV(I)/PEXP(I)*100.D0
      TOT=TOT+DABS(ERR(I))
      DR(I)=VC/V(I)
      RRHO(I)=1.0D03/VI(I,J)/RHOS
      WRITE(6,119)  I,PRES(I),V(I),RRHO(I),PEXP(I),
     1PCAL(I),DEV(I),ERR(I)
119 FORMAT(1X,I3,F10.2,7F10.4)
118 CONTINUE
116 CONTINUE
      AVG=TOT/TERM
      WRITE(6,201) AVG
201 FORMAT(//30H AVERAGE PERCENTAGE ERROR IS =,F10.4//)
      STOP
      END
      SUBROUTINE PATERN(NP,P,STEP,NPASS,IO,AB,BB)
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      DIMENSION P(NP),STEP(NP)
      DIMENSION B1(4),B2(4),T(4),S(4),AB(4),BB(4)
      IOF=6
      NRD=NPASS
      L=1
      ICK=2
      ITTER=0
      DO 5 I=1,NP
      B1(I)=P(I)
      B2(I)=P(I)
      T(I)=P(I)
    5 S(I)=STEP(I)*10.
      CALL BOUNDS(P,IOUT,AB,BB,NP)
      IF(IOUT.LE.0) GO TO 10
      IF(IO.LE.0) GO TO 6
      WRITE(IOF,1005)
      WRITE(IOF,1000)(J,P(J),J=1,NP)
```

```
 6 GO TO 999
10 CALL DCFI(P,C1)
   IF(IO.LE.1) GO TO 11
   WRITE(IOF,1001) ITTER,C1
   WRITE(IOF,1000) (J,P(J),J=1,NP)
11 DO 79 INRD=1,NRD
   DO 12 I=1,NP
12 S(I)=S(I)/10.
   IF(IO.LE.1) GO TO 20
   WRITE(IOF,1003)
   WRITE(IOF,1000) (J,S(J),J=1,NP)
20 IFAIL=0
   DO 30 I=1,NP
   IC=0
21 P(I)=T(I)+S(I)
   IC=IC+1
   CALL BOUNDS(P,IOUT,AB,BB,NP)
   IF(IOUT.GT.0) GO TO 23
   CALL DCFI(P,C2)
   L=L+1
   IF(IO.LT.3) GO TO 22
   WRITE(IOF,1002) L,C2
   WRITE(IOF,1000) (J,P(J),J=1,NP)
22 IF(C1-C2) 23,23,25
23 IF(IC.GE.2) GO TO 24
   S(I)=-S(I)
   GO TO 21
24 IFAIL=IFAIL+1
   P(I)=T(I)
   GO TO 30
25 T(I)=P(I)
   C1=C2
30 CONTINUE
   IF(IFAIL.LT.NP) GO TO 35
   IF(ICK.EQ.2) GO TO 90
   IF(ICK.EQ.1) GO TO 35
   CALL DCFI(T,C2)
   L=L+1
   IF(IO.LT.3) GO TO 31
   WRITE(IOF,1002) L,C2
   WRITE(IOF,1000) (J,T(J),J=1,NP)
31 IF(C1-C2) 32,34,34
32 ICK=1
   DO 33 I=1,NP
   B1(I)=B2(I)
   P(I)=B2(I)
33 T(I)=B2(I)
   GO TO 20
34 C1=C2
35 IB1=0
   DO 39 I=1,NP
   B2(I)=T(I)
   IF(DABS(B1(I)-B2(I)).LT.(DABS(S(I))*.01)) IB1=IB1+1
39 CONTINUE
   IF(IB1.EQ.NP) GO TO 90
   ICK=0
   ITTER=ITTER+1
   IF(IO.LT.2) GO TO 40
   WRITE(IOF,1001) ITTER,C1
   WRITE(IOF,1000) (J,T(J),J=1,NP)
```

```
   40 SJ=1.
      DO 45 II=1,11
      DO 42 I=1,NP
      T(I)=B2(I)+SJ*(B2(I)-B1(I))
   42 P(I)=T(I)
      SJ=SJ-.1
      CALL BOUNDS(T,IOUT,AB,BB,NP)
      IF(IOUT.LT.1) GO TO 46
      IF(II.EQ.11) ICK=1
   45 CONTINUE
   46 DO 47 I=1,NP
   47 B1(I)=B2(I)
      GO TO 20
   90 DO 91 I=1,NP
   91 T(I)=B2(I)
   99 CONTINUE
      DO 100 I=1,NP
  100 P(I)=T(I)
      COST=C1
      IF(IO.LE.0) GO TO 999
      WRITE(IOF,1004) L,C1
      WRITE(IOF,1000) (J,P(J),J=1,NP)
  999 CONTINUE
      RETURN
 1000 FORMAT(1X,5(I7,E13.6)/)
 1001 FORMAT(//1X,13HITERATION NO.,I5/5X,5HCOST=,E15.6,20X,
     110HPARAMETERS)
 1002 FORMAT(10X,3HNO.,I4,8X,5HCOST=,E15.6)
 1003 FORMAT(/1X,28HSTEP SIZE FOR EACH PARAMETER)
 1004 FORMAT(1X,13HANSWERS AFTER,I3,2X,22HFUNCTIONAL EVALUATIONS
     1//5X,5HCOST=,E15.6,20X,18HOPTIMAL PARAMETERS)
 1005 FORMAT(1X,35HINITIAL PARAMETERS OUT OF BOUNDS    )
      END
      SUBROUTINE BOUNDS(P,IOUT,AB,BB,NP)
      REAL*8 AB(4),BB(4),P(4)
      IOUT=0
      DO 1 I=1,NP
    1 IF(P(I).LE.AB(I) .OR. P(I).GT.BB(I)) IOUT=1
      RETURN
      END
      SUBROUTINE DCFI(P,SUM)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION VI(8,34),PI(8,34),RHO(8)
      DIMENSION P(4),TEMP(34),PEXP(8),PCAL(8)
      COMMON/DATA/TEMP,VI,PI,PEXP,PCAL,VC
      COMMON/COND/NP,NJ,NN,TERM
      COMMON/PRINT/PPEX(8,34),PPCA(8,34)
      COMMON/PARAM/RHOS,DCFS,TS
      RHOS=P(1)
      DCFS=P(2)
      TS=P(3)
      RK=0.0831434D0
      SUM=0.0D0
      TERM=0.0D0
      DO 6 J=1,NJ
      TT=TS/TEMP(J)
      NN=0
      DO 10 K=1,8
      IF(VI(K,J).LT.1.0D0) GO TO 10
      NN=NN+1
```

```
      RHO(NN)=1.0D03/VI(K,J)
      DR=RHO(1)/RHOS
      PEXP(NN)=PI(K,J)
      PR=PEXP(1)
   10 CONTINUE
      DO 13 I=2,NN
      DN=RHO(I)/RHOS
      TERM=TERM+1
      A0=0.98642D01-0.10191D02*TT-0.15356D01*TT*TT
      A1=-0.28465D02+0.30864D02*TT+0.60294D01*TT*TT
      A2=0.27542D02-0.32898D02*TT-0.87130D01*TT*TT
      A3=-0.82606D01+0.12737D02*TT+0.40170D01*TT*TT
      B0=RHOS*(DN-DR)*RK*TS/TT
      B1=DN+DR
      B2=DN*DN+DN*DR+DR*DR
      B3=DN*DN*DN+DN*DN*DR+DN*DR*DR+DR*DR*DR
      C0=A0+A1*B1/2.0D0+A2*B2/3.0D0+A3*B3/4.0D0
      PCAL(I)=PR+B0*(1.0D0-DCFS*C0)
      SUM=SUM+(PCAL(I)-PEXP(I))**2
      PPEX(I,J)=PEXP(I)
      PPCA(I,J)=PCAL(I)
   13 CONTINUE
    6 CONTINUE
      SUM=DSQRT(SUM/(TERM-1.0D0))
      RETURN
      END
```

```
C     CORRESPONDING STATES CORRELATION OF THE VOLUMETRIC
C     PROPERTIES OF COMPRESSED LIQUID MIXTURES.
C     MAIN PROGRAM
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION P(4),STEP(4),AB(4),BB(4),NJ(8),NAME(20)
      DIMENSION TC(3),VC(3),TS(3),VS(3),CS(3)
      DIMENSION TCM(8),VCM(8),TSM(8),RHOS(8),DCFS(8)
      DIMENSION XI(8,3),TEMP(24,8),TR(24,8),RRHO(8)
     1,PEXP(8),PCAL(8),DEV(8),ERR(8)
      DIMENSION VI(8,24,8),CI(8,24,8),PI(8,24,8)
     1,VII(8),CII(8),PII(8),V(8),PRES(8)
      COMMON/DATA/TEMP,VI,PI,PEXP,PCAL
      COMMON/COND/NP,NC,NI,NJ,NN,TERM
      COMMON/PRINT/PPEX(8,24,8),PPCA(8,24,8)
      COMMON/PARAM/TCM,VCM,TSM,RHOS,DCFS
      COMMON/CRIT/XI,TC,VC,TS,VS,CS
      READ(5,13) NAME
   13 FORMAT(20A4)
      READ(5,101) NP,IO
  101 FORMAT(2I2)
      READ(5,102) NPASS,(P(I),I=1,NP),(STEP(I),I=1,NP)
      READ(5,103) (AB(I),I=1,NP),(BB(I),I=1,NP)
  102 FORMAT(I2,6F10.0)
  103 FORMAT(3X,6F10.0)
      WRITE(6,104)
  104 FORMAT(1X,'PATTERN SEARCH ESTIMATION OF PARAMETERS FROM
     1DCFI DATA'/1X,'CONTROL PARAMETERS WERE SET AS FOLLOWS-'/)
      WRITE(6,105) NP,IO
  105 FORMAT(1X,5H  NP=,I2/1X,5H  IO=,I2)
      WRITE(6,106) NPASS
  106 FORMAT(1X,15HNUMBER OF PASS=,I2)
      WRITE(6,107)
  107 FORMAT(1X,18HINITIAL PARAMETERS)
      WRITE(6,108) (I,P(I),I=1,NP)
  108 FORMAT(1X,I2,F10.3)
      WRITE(6,109)
  109 FORMAT(1X,12HSIZE OF STEP)
      WRITE(6,110) (I,STEP(I),I=1,NP)
  110 FORMAT(1X,I2,F10.3)
      WRITE(6,111)
  111 FORMAT(1X,30HLOWER LIMITS OF THE PARAMETERS)
      WRITE(6,112) (I,AB(I),I=1,NP)
  112 FORMAT(1X,I2,F10.3)
      WRITE(6,113)
  113 FORMAT(1X,30HUPPER LIMITS OF THE PARAMETERS)
      WRITE(6,114) (I,BB(I),I=1,NP)
  114 FORMAT(1X,I2,F10.3)
      READ(5,1) NC
    1 FORMAT(I2)
      WRITE(6,2) NC
    2 FORMAT(/1X,'NO. OF COMPONENTS= ',I2/)
      READ(5,3) (TC(I),VC(I),I=1,NC)
      READ(5,3) (TS(I),VS(I),CS(I),I=1,NC)
    3 FORMAT(8F10.0)
      READ(5,1) NI
      DO 100 II=1,NI
      READ(5,3) (XI(II,I),I=1,NC)
      READ(5,1) NJ(II)
      DO 200 JJ=1,NJ(II)
      READ(5,3) TEMP(JJ,II)
```

```
      READ(5,3) VII,CII,PII
      DO 300 KK=1,8
      VI(KK,JJ,II)=VII(KK)
      CI(KK,JJ,II)=CII(KK)
      PI(KK,JJ,II)=PII(KK)
  300 CONTINUE
  200 CONTINUE
  100 CONTINUE
      CALL PATERN(NP,P,STEP,NPASS,2,AB,BB)
      CALL DCFI(P,SUM)
      WRITE(6,301) NAME
  301 FORMAT(///17H  THE SYSTEM IS : 20A4///)
      TOT=0.0D0
      DO 115 II=1,NI
      WRITE(6,8) (XI(II,I),I=1,NC-1)
    8 FORMAT(///1X,' X1=',2F9.5)
      WRITE(6,9) TCM(II),VCM(II),TSM(II),RHOS(II),DCFS(II)
    9 FORMAT('  TCM=',F8.3,' K''/''  VCM=',
     1F8.3,  ' CC/GMOL''/''  T*=',F9.3,' K'
     1/'  D*=',F8.4,' GMOL/L''/''  C*=',F9.4//)
      DO 116 JJ=1,NJ(II)
      TR(JJ,II)=TEMP(JJ,II)/TSM(II)
      WRITE(6,10) TEMP(JJ,II),TR(JJ,II)
   10 FORMAT(//1X,'FOR THE ISOTHERM AT',  F7.2,  ' DEG.  K,',
     1'THE REDUCED TEMPERATURE IS',F7.4)
      WRITE(6,14) PI(1,JJ,II),VI(1,JJ,II)
   14 FORMAT(//1X,'THE REFERENCE PRESSURE IS',  F8.4,  '
     1 BAR,',  'THE REFERENCE MOLAR VOLUME IS',F9.4//)
      WRITE(6,11)
   11 FORMAT(2X,3HNO.,3X,5HP,BAR,3X,8HV,CC/MOL,5X,4HD/D*,4X,
     15HP,EXP,5X,5HP,CAL,7X,4HDEV.,5X,5H% ERR/)
      DO 117 KK=2,8
      PRES(KK)=PI(KK,JJ,II)
      V(KK)=VI(KK,JJ,II)
      PEXP(KK)=PPEX(KK,JJ,II)
      PCAL(KK)=PPCA(KK,JJ,II)
      IF(DABS(PEXP(KK)).LT.1.0D-5) GO TO 117
      DEV(KK)=PEXP(KK)-PCAL(KK)
      ERR(KK)=DEV(KK)/PEXP(KK)*100.D0
      TOT=TOT+DABS(ERR(KK))
      RRHO(KK)=1.0D03/VI(KK,JJ,II)/RHOS(II)
      WRITE(6,12) KK,PRES(KK),V(KK),RRHO(KK),PEXP(KK),
     1PCAL(KK),DEV(KK),ERR(KK)
   12 FORMAT(1X,I3,F10.2,7F10.4)
  117 CONTINUE
  116 CONTINUE
  115 CONTINUE
      AVG=TOT/TERM
      WRITE(6,201) AVG
  201 FORMAT(//30H AVERAGE PERCENTAGE ERROR IS =,F10.4//)
      STOP
      END
      SUBROUTINE PATERN(NP,P,STEP,NPASS,IO,AB,BB)
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      DIMENSION P(NP),STEP(NP)
      DIMENSION B1(4),B2(4),T(4),S(4),AB(4),BB(4)
      IOF=6
      NRD=NPASS
      L=1
      ICK=2
```

```
      ITTER=0
      DO 5 I=1,NP
      B1(I)=P(I)
      B2(I)=P(I)
      T(I)=P(I)
    5 S(I)=STEP(I)*10.
      CALL BOUNDS(P,IOUT,AB,BB,NP)
      IF(IOUT.LE.0) GO TO 10
      IF(IO.LE.0) GO TO 6
      WRITE(IOF,1005)
      WRITE(IOF,1000)(J,P(J),J=1,NP)
    6 GO TO 999
   10 CALL DCFI(P,C1)
      IF(IO.LE.1) GO TO 11
      WRITE(IOF,1001) ITTER,C1
      WRITE(IOF,1000) (J,P(J),J=1,NP)
   11 DO 99 INRD=1,NRD
      DO 12 I=1,NP
   12 S(I)=S(I)/10.
      IF(IO.LE.1) GO TO 20
      WRITE(IOF,1003)
      WRITE(IOF,1000) (J,S(J),J=1,NP)
   20 IFAIL=0
      DO 30 I=1,NP
      IC=0
   21 P(I)=T(I)+S(I)
      IC=IC+1
      CALL BOUNDS(P,IOUT,AB,BB,NP)
      IF(IOUT.GT.0) GO TO 23
      CALL DCFI(P,C2)
      L=L+1
      IF(IO.LT.3) GO TO 22
      WRITE(IOF,1002) L,C2
      WRITE(IOF,1000) (J,P(J),J=1,NP)
   22 IF(C1-C2) 23,23,25
   23 IF(IC.GE.2) GO TO 24
      S(I)=-S(I)
      GO TO 21
   24 IFAIL=IFAIL+1
      P(I)=T(I)
      GO TO 30
   25 T(I)=P(I)
      C1=C2
   30 CONTINUE
      IF(IFAIL.LT.NP) GO TO 35
      IF(ICK.EQ.2) GO TO 90
      IF(ICK.EQ.1) GO TO 35
      CALL DCFI(T,C2)
      L=L+1
      IF(IO.LT.3) GO TO 31
      WRITE(IOF,1002) L,C2
      WRITE(IOF,1000) (J,T(J),J=1,NP)
   31 IF(C1-C2) 32,34,34
   32 ICK=1
      DO 33 I=1,NP
      B1(I)=B2(I)
      P(I)=B2(I)
   33 T(I)=B2(I)
      GO TO 20
   34 C1=C2
```

```
 35 IB1=0
    DO 39 I=1,NP
    B2(I)=T(I)
    IF(DABS(B1(I)-B2(I)).LT.(DABS(S(I))*.01)) IB1=IB1+1
 39 CONTINUE
    IF(IB1.EQ.NP) GO TO 90
    ICK=0
    ITTER=ITTER+1
    IF(IO.LT.2) GO TO 40
    WRITE(IOF,1001) ITTER,C1
    WRITE(IOF,1000) (J,T(J),J=1,NP)
 40 SJ=1.
    DO 45 II=1,11
    DO 42 I=1,NP
    T(I)=B2(I)+SJ*(B2(I)-B1(I))
 42 P(I)=T(I)
    SJ=SJ-.1
    CALL BOUNDS(T,IOUT,AB,BB,NP)
    IF(IOUT.LT.1) GO TO 46
    IF(II.EQ.11) ICK=1
 45 CONTINUE
 46 DO 47 I=1,NP
 47 B1(I)=B2(I)
    GO TO 20
 90 DO 91 I=1,NP
 91 T(I)=B2(I)
 99 CONTINUE
    DO 100 I=1,NP
100 P(I)=T(I)
    COST=C1
    IF(IO.LE.0) GO TO 999
    WRITE(IOF,1004) L,C1
    WRITE(IOF,1000) (J,P(J),J=1,NP)
999 CONTINUE
    RETURN
1000 FORMAT(1X,5(I7,E13.6)/)
1001 FORMAT(//1X,13HITERATION NO.,I5/5X,5HCOST=,E15.6,20X,
   110HPARAMETERS)
1002 FORMAT(10X,3HNO.,I4,8X,5HCOST=,E15.6)
1003 FORMAT(/1X,28HSTEP SIZE FOR EACH PARAMETER)
1004 FORMAT(1X,13HANSWERS AFTER,I3,2X,22HFUNCTIONAL EVALUATIONS
   1//5X,5HCOST=,E15.6,20X,18HOPTIMAL PARAMETERS)
1005 FORMAT(1X,35HINITIAL PARAMETERS OUT OF BOUNDS    )
    END
    SUBROUTINE BOUNDS(P,IOUT,AB,BB,NP)
    REAL*8 AB(4),BB(4),P(4)
    IOUT=0
    DO 1 I=1,NP
  1 IF(P(I).LE.AB(I) .OR. P(I).GT.BB(I)) IOUT=1
    RETURN
    END
    SUBROUTINE DCFI(P,SUM)
    IMPLICIT REAL*8(A-H,O-Z)
    DIMENSION TC(3),VC(3),TS(3),VS(3),CS(3),NJ(8)
    DIMENSION TCM(8),VCM(8),TSM(8),VSM(8),RHOS(8),DCFS(8)
    DIMENSION VI(8,24,8),PI(8,24,8),DIJ(3,3),RHO(8)
    DIMENSION P(4),XI(8,3),TEMP(24,8),PEXP(8),PCAL(8)
    COMMON/DATA/TEMP,VI,PI,PEXP,PCAL
    COMMON/COND/NP,NC,NI,NJ,NN,TERM
    COMMON/PRINT/PPEX(8,24,8),PPCA(8,24,8)
```

```
      COMMON/PARAM/TCM, VCM, TSM, RHOS, DCFS
      COMMON/CRIT/XI, TC, VC, TS, VS, CS
      DIJ(1,2)=P(1)
      DIJ(2,1)=DIJ(1,2)
      DIJ(1,1)=0.D0
      DIJ(2,2)=0.D0
      SUM=0.D0
      TERM=0.D0
      DO 1 II=1,NI
      TCM(II)=0.D0
      VCM(II)=0.D0
      TSM(II)=0.D0
      VSM(II)=0.D0
      DCFS(II)=0.D0
      DO 2 I=1,NC
      TCM(II)=TCM(II)+XI(II,I)*TC(I)
      TSM(II)=TSM(II)+XI(II,I)*TS(I)
    2 DCFS(II)=DCFS(II)+XI(II,I)*CS(I)
      DO 3 I=1,NC
      DO 3 J=1,NC
      VCM(II)=VCM(II)+XI(II,I)*XI(II,J)*(((VC(I)+VC(J))/2.D0)
    3 VSM(II)=VSM(II)+XI(II,I)*XI(II,J)*(((VS(I)+VS(J))/2.D0)
     1*(1.D0-DIJ(I,J)))
      RK=0.0831434D0
      DO 6 JJ=1,NJ(II)
      TT=TSM(II)/TEMP(JJ,II)
      NN=0
      DO 10 KK=1,8
      IF(VI(KK,JJ,II).LT.1.0D0) GO TO 10
      NN=NN+1
      RHO(NN)=1.0D03/VI(KK,JJ,II)
      RHOS(II)=1.0D03/VSM(II)
      DR=RHO(1)/RHOS(II)
      PEXP(NN)=PI(KK,JJ,II)
      PR=PEXP(1)
   10 CONTINUE
      DO 13 KK=2,NN
      DN=RHO(KK)/RHOS(II)
      TERM=TERM+1
      A0=0.98642D01-0.10191D02*TT-0.15356D01*TT*TT
      A1=-0.28465D02+0.30864D02*TT+0.60294D01*TT*TT
      A2=0.27542D02-0.32898D02*TT-0.87130D01*TT*TT
      A3=-0.82606D01+0.12737D02*TT+0.40170D01*TT*TT
      B0=RHOS(II)*(DN-DR)*RK*TSM(II)/TT
      B1=DN*DR
      B2=DN*DN+DN*DR+DR*DR
      B3=DN*DN*DN+DN*DN*DR+DN*DR*DR+DR*DR*DR
      C0=A0+A1*B1/2.0D0+A2*B2/3.0D0+A3*B3/4.0D0
      PCAL(KK)=PR+B0*(1.0D0-DCFS(II)*C0)
      SUM=SUM+(PCAL(KK)-PEXP(KK))**2
      PPEX(KK,JJ,II)=PEXP(KK)
      PPCA(KK,JJ,II)=PCAL(KK)
   13 CONTINUE
    6 CONTINUE
    1 CONTINUE
      SUM=DSQRT(SUM/(TERM-1.0D0))
      RETURN
      END
```

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